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Batteries & Energy Storage Technology Winter 2014

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Batteries and Energy Storage Technology magazine (ISSN: 1741-8666) is published four times a year (January, April, July and October), by Energy Storage Publishing Ltd., 70 Goring Road, Worthing BN12 4AB ENGLAND and distributed in the USA by Mail Right International, 1637 Stelton Road B4, Piscataway, NJ 08854. Periodicals Postage Paid at New Brunswick, NJ.

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subscriptions@bestmag.co.uk The subscription rate per annum is £100, or £50 for digital only. (see www.bestmag.co.uk for details)

POSTMASTER

Send U.S. address changes to BEST C/o 1637 Stelton Road, B-4, Piscataway NJ 08854

Cover pic: BBC/Charles Birchmore PRINTED IN ENGLAND



appy New Year and welcome to the first issue of BEST in 2014. I shall not make predictions for the year ahead except for one: battery companies will continue to exaggerate the technical benefits of their products.

But not quite so much, perhaps, as Envia Systems, which claimed its 45A lithium NMC cells had an energy density of 400 Wh/kg at a cost of \$150/kWh.

As we detail on page 12, Envia is now the subject of a lawsuit which alleges the company was founded using stolen intellectual property. Envia denies the allegations.

Amazingly, GM trusted Envia, and a signed a contract requiring the latter to produce— within less than a year— a battery generating c.350 Wh/kg that could last 1 000 charge-discharge cycles.

A fabulous article published in December written by American journalist Steve LeVine, *The Mysterious Story of the Battery Startup That Promised GM a 200-mile Electric Car*, painfully lays bare GM's mistakes.

Even a cursory glance at the validated performance test data, which secured Envia \$4m (all \$ are US\$ unless otherwise shown) funding under the US DOE's ARAP-E competition, would have showed GM the performance of the cells dropped dramatically.

While Envia's claim was accurate— energy density of 378 to 426 Wh/kg has been achieved and had been put through 409 charge-discharge cycles— by the 25th cycle, energy density reduced to 290 Wh/kg.

At the 100th cycle, it was at 266 Wh/kg. At the 200th, it was below 250 Wh/kg, and by the 300th, it was 237 Wh/kg. By the last charge-discharge cycle— the 409th— the cell's energy density had fallen to 222 Wh/kg, just 55% of what Envia claimed.

How could GM have been so dumb? One theory suggested to us is that in desperation to provide the Chevy Volt with a battery pack with the range of a Tesla at a fraction of the cost, GM's senior management allowed the business managers to overrule the engineers.

The only other possible reason is GM staff and managers' experience in lithium-ion cell manufacturing and testing was inadequate. Yet GM really ought to have known better given its substantial electrochemical expertise and its EV team has been producing electric cars since the EV-1 first hit the streets in 1996.

Whatever the truth of the matter, GM's electric vehicle reputation has been damaged further by the Envia debacle. As for Envia, the case continues, as they say.

LeVine quotes Jeff Dahn, head of battery research at Canada's Dalhousie University: "With battery people," Dahn said, "You have to make sure that a statement applies to all parts of the sentence." Too true.

Enjoy the issue



Tim Probert

Editor

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Looking back, and forward

hristmas and the New Year are periods of reflection and predictions. After several years of economic downturn there are growing noises from those in the know that recovery is well under way and growth has returned in the USA and the UK.

While, generally speaking, things still look worrying in Europe, in Asia the downturn simply didn't happen. Asian factories are churning out the most of the hardware for avid western consumers, as well as a rapidly growing middle class at home.

What of the dark continent of Africa? In a slow news week at the beginning of January, the BBC World Service and the BBC domestic radio flagship programme 'Today'

teamed up to report from Lagos, Nigeria, suggesting that the country would become a superpower in the next 15 years.

The portents are there. A young population of 192m, not to mention 10% of the world's oil and gas reserves.

On the downside, the country's power utilities are a mess, the state of the education system is pitiful. But, still, that's 250 million avid consumers by 2030.

According to the US National Intelligence Council global trends report, it's not just Nigeria whose fortunes will change. Colombia, Indonesia, South Africa and Turkey will become especially



important to the global economy, the report says.

And one can predict with reasonably confidence that countries on those nations' borders will also gain.

How does any of this translate into the world of batteries?

All for the good. The growing car parks will be good for traditional lead-acid sales and, inevitably, growing industrial battery sales as these countries build infrastructure. Add plenty of opportunity for aftermarket sales into the mix and one can expect a new clutch of independent battery manufacturers. What of the old world of the USA, Europe and Japan? Is managed decline the only message? Ageing populations are a bigger worry perhaps than ageing infrastructure.

The retired elderly do not produce; consume more resources as lifespan increases and create a burden on the young as their healthcare costs rise and more taxes have to be raised for care. Meanwhile, productivity gains cut employment opportunities for those young enough to be working and suitably skilled to do so.

Batteries aren't ever going away. But where the industry will be headquartered, where research happens, where trade events are staged and

where the most important markets are will look very different by the time this writer hangs up his charging leads in the next ten years. *Scary?* You bet. 🗘

on would

Gerry Woolf - Publisher

Let's hear from you

Got an opinion on the above or anything else? Then share it. If it's battery standards or the answer to the ultimate question in the universe, BEST's readers would like to know. **Contact: tim@energystoragepublishing.com**



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Fraud accusations swamp Envia

Envia Systems, a developer of automotive lithium-ion batteries, has been accused of stealing what it had called the proprietary technology in its product.

The California-based company boasted a lithium-ion automotive battery with greater energy density than any competitor thus attracting a deal from GM and funding from the US Department of Energy's Advanced Research Projects Agency for Energy (ARPA-E). Envia is now at the centre of a legal battle after being accused by former employees of intellectual property theft from another Californian lithium-ion developer NanoeXa.

The lawsuit, filed by four Envia executives on 22 November 2013, claims the founder of the company, Sujeet Kumar, stole the intellectual property from NanoeXa – where he had previously worked. Envia has dismissed it as a slur from disgruntled former employees.

Michael Pak, founder, CEO and president of NanoeXa, is the plaintiff in the case. NanoeXa had licensed a patent from Argonne National Laboratory relating to a nickel manganese cobalt (NMC) cathode. Kumar was the main electro-engineer at NanoeXa, a position he left a year after the NMC was obtained to set up his own lithium-ion battery start-up company.

At Envia, the NMC cathode was combined with a silicon anode that resulted in a battery with an energy density of 400Wh/kg.



For this, Envia had received \$4m grant from ARPA-E and \$1m from the California Energy Commission to develop the technology to bring the technology from prototype to a commercial.

Envia had licensed a separate patent agreement from Argonne, but Pak has alleged that Kumar is using his knowledge of developing NMC that he gained at NanoeXa during the 12 months before resigning. It is alleged Kumar downloaded details of developing NMC along with NanoeXa's marketing strategy onto a personal storage device before leaving the company.

The silicon anode material has also been alleged to be the intellectual property of another company— Shin-Etsu, a Japanese supplier. Envia claimed the anode is propriatery because of the developments made in-house, but the core of technology that enabled the energy density is available for anyone to license from Shin-Etsu.

Thanks to this 'too good to be true' battery, Envia entered a deal with GM in November 2012 to license the technology for automotive batteries. At this stage it was understood Envia owned or was legally able to license the technology.

The proposed contract was for Envia to supply a cathode for GM's Volt from 2015 onwards, as well as a complete battery for a different vehicle from 2016. Envia would receive up to \$8m a year in the deal as well as royalties on each car.

The company hoped to find a large company to buy it out

but despite its promising deal with GM, potential buyers saw flaws with the technology and failed to secure a buyer.

The promised performance of 400wh/kg energy density was claimed to last for 300 charge/discharge cycles. Although the tested batteries did provide that energy density the performance dropped off long before 300 cycles.

Under extensive testing by GM it became clear the energy density performance of the prototype could not be replicated and GM cancelled the deal.

Atul Kapadia is the former CEO, who had invested in the company to get it off the ground. He was let go from Envia in August 2013 following internal rows that included the proprietary nature of the anode material and the claims Envia was making about it. Part of his role in the company had been to quash a lawsuit brought against Envia by NanoeXa in 2012.

Following his termination, Kapadia filed a civil case against Envia and Kumar. It alleged fraud— largely based on the previous lawsuite brought by NanoeXa— and wrongful termination.

Envia Systems denies that Kumar stole the technology or trade secrets from NanoeXa. In a statement the company said: "The allegations are baseless.

"The evidence will show that the plaintiffs' lawsuit is nothing more than spurious allegations of three disgruntled former employees." 🗘

Fisker caught in bankruptcy battle

Risker Automotive entered into Chapter 11 bankruptcy proceedings in November 2013 following mounting debts. A bidding war for its assets, and debts, has begun between Wanxiang America and Hybrid Tech Holdings – a newly-formed Hong Kong-based company.

A \$25m deal was nearly complete for Hybrid Tech to buy Fisker's assets and take over a defaulted Department of Energy loan. However, before the deal was sealed Wanxiang, a Chinese autoparts maker, made a rival offer.

It was alleged by Fisker's unsecured creditors in the bankruptcy court that Hybrid's bid was unlawful because a former Fisker board member became the CEO of Hybrid Tech on the day of the deal.

This led the creditors to request an auction of Fisker's assets with Wanxiang playing the stalking horse bidder.

In court papers the creditors made the statement: "The debtors' proposed sale to Hybrid Tech Holdings LLC, as well as the related bid procedures, are improper and will not serve the best interests of the debtors' creditors and parties in interest."

The bankruptcy court judge in Delaware, US, ordered an auction of assets for the benefit of creditors. Following



this both bidders stepped up their offers. Wanxiang made a bid on 10 January of \$37m and a 20% share ownership for the creditors. Hybrid Technology beat this offer on 13 January with an offer of \$55m.

Wanxiang America bought A123 in January 2013 for \$256.6m. Following the sale, Wanxiang terminated A123's supply deal to Fisker leaving ill feeling from Fisker toward Wanxiang.

Fisker's creditors have argued that as Wanxiang already owns a major component of Fisker's car – the battery – it makes sense to also acquire the electric carmaker. At the time of going to press, the auction is expected to take place in February. •

Polypore settles patent claim against Sumitomo

elgard parent Polypore International has reached a settlement in a patent infringement case against rival Sumitomo Corp of Japan.

Charlotte, USA-based Polypore has licensed Sumitomo to use its batteryseparator coating technology in separators Sumitomo produces for companies such as Panasonic. The company says the settlement "ends all outstanding worldwide litigation between the two companies" over what Polypore contends was Sumitomo's pirating of its intellectual property.

Polypore said the "financial terms of the Agreement include

an up-front payment to Polypore as well as recurring royalties."

"This agreement confirms the integrity of our intellectual property around ceramic coating of separators for lithium-ion batteries," says Polypore CEO Robert Toth. "In addition to the financial consideration of the licensing arrangement, we are pleased that this agreement establishes the opportunity for Polypore and Sumitomo to work together to address growing market needs, which we expect to benefit both companies."

In February 2013, Celgard filed a suit in US District Court. It asked the judge to stop Sumitomo from manufacturing the challenged batteryseparator parts. It also asked the judge to order payment of royalty fees and unspecified damages.

The licensing agreement with Sumitomo could mean that Tesla Motors will be using Polypore technology in its electric cars, adding strength to Polypore's automotive position currently thought to be buttressed by placement on the Nissan Leaf. In a report, Stifel Nicolaus analyst Jeffery Osborne called it good news for Polypore. "We believe Tesla ... is one of Panasonic's largest customers using the format of battery mentioned in the filing," Osborne wrote. "While we have no way of quantifying the impact of this agreement, we view it as a long term positive for the company as they maintain their leadership in the market." •

EV sales rocket in France

The France sales of electric cars rose by 55% from 5 663 in 2012 to 8 770 in 2013. The Nissan Zoe was the best selling model with sales of 5 511. Electric van sales increased by 42% to 5 175 sold in 2013. 46785 new hybrids were registered on the roads- an increase of 60% on the previous year.

Microporous independent after \$120m private equity acquisition

Manufacturer of separators for leadacid batteries, has been fully acquired by New York-based private equity firm Seven Mile Capital Partners for \$120m.

Microporous is now a fully independent company and will compete directly with the Daramic division of its prior parent company, Polypore International, Inc. Polypore sold the business pursuant to a divestiture order from the Federal Trade Commission.

Microporous' product line includes the Flex-Sil, Ace-Sil, and CellForce brands in addition to PE separators for industrial and PE automotive applications. In particular, the company will be the largest producer of separators for deep-cycle flooded lead-acid batteries. The new CEO and President of Microporous is Jean-Luc Koch, who has 16 years of worldwide experience in the lead-acid battery industry. Koch said: "A primary goal within this first year is to reinforce our customer relationships to be able to respond to their needs. We will also aggressively compete in the marketplace to add new customers." Steve McDonald, vice president of sales, said: "A clear message we've heard from customers is that they want Microporous to return with a focus on improving technology through R&D and be more customer-centric.

"For the past six years as part of Daramic, we weren't given the opportunity to work on R&D projects with our customers. That will change moving forward."

Atraverda is back with uprated bipolar battery

British bipolar battery maker Atraverda is launching a new 24V lead-acid battery in the second quarter of 2014.

The new battery is an uprated version of its first 24V, 15Ah bipolar battery, hundreds of which have been trialled, mostly for electric wheelchairs and golf carts. Following feedback from its clients wanting a product with higher volumetric energy density, Atraverda is to launch a 24V, 18Ah battery by summer 2014.

Bipolar batteries replace standard lead-acid batteries' multiple layers of grids, paste and separators with a single layer of conductive material. By removing 40% of lead, higher energy density is achieved at a claimed 20% lower manufacturing cost versus conventional lead-acid batteries.

Bipolar batteries also use the entire surface area between

each cell to transfer current and cause less stress, improving lifetime and performance.

The lead-acid battery industry has been trying to

crack the bipolar nut for the past 30 years. Effective bipolar batteries require material between cells that can effectively

transmit electrons while being impervious to highly corrosive sulphuric acid to prevent cell leakage.

Atraverda employs its patented ceramic composite Ebonex, which consists of a suboxide of titanium dioxide, commonly used as a pigment in white paint. Ebonex is the base material in the ceramic substrate, which acts as both electrode and cell separator. Tony Davies, chief executive officer, told BESTmag: "Over the past ten years, bipolar

batteries have had a history of high failure rate due to leakage. We have developed to the level where we have extremely leak-proof

batteries and conductive cathodes between the cells."

Atraverda is targeting its bipolar battery at the \$3bn a year e-bike market in Asia. Davies said the Abertillerybased firm was on the verge of announcing a joint venture with a major Asian battery company to commence high-volume production for e-bikes. Davies was not prepared at this stage to disclose the company's name, but said it had one of "the biggest factories in the world".

The long-term goal is to produce a 48V, 30Ah 'core product' for telecoms, light electric vehicles and the energy storage market.

Atraverda is currently holding a funding round to scale up production capacity of its pilot line at its South Wales headquarters. The firm had previously spent many months trying to secure funding to continue production but were let down by an investor late in 2012.

The company withdrew before the deal was finalised and the board of directors were forced to file for administration in December 2012. After failing to secure working capital to continue production had to lay off 37 of 44 employees. Only a core staff in technical roles remains. •



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Yuasa targets UPS market with high capacity VRLA battery

VRLA batteries for use in UPS systems with the addition of a high capacity 12V model, the SWL4250.

The battery is suited to high discharge rate applications, making it ideal for UPS applications. It has a nominal ten hour rate capacity of 140Ah to 10.8V at 20°C with ten minute rate constant power of 4,250W to 9.6V at 20°C. In a standby function the life expectancy is claimed to be ten years at optimal operating conditions.

The battery has been designed to operate at temperatures between -15 to +50°C (charging) and -20 to +60°C (discharging). The optimum storage temperature in fully charged condition is from -20 to +50°C. The SWL4250 features a UL94HB ABS case material as standard with flame retardant option available for UL94V0 applications. The 49kg battery measures 341 x 173 x 281mm. •





Formula E races toward starting line

F ormula E, the zerocarbon race series beginning this September, has publicly demonstrated the all-electric race car that will be used by all teams in the first race series. F1 driver Lucas di Grassi drove the Spark-Renault_o1E on the streets of Las Vegas.

Spark Racing and Renault have developed the car, with a drivetrain constructed by McClaren and 200kw batteries supplied by F1 veterans Williams Advanced Engineering. The Spark-Renault SRT_01E will be a zero-emission single-seater racecar that showcases the most advanced EV technology that can be developed for application to passenger vehicles.

From the second season teams will be encouraged to develop and race their own custom cars that adhere to

The race calendar is as follows:

- Round 1 Beijing, China, 13 September 2014
- Round 2 Putrajaya, Malaysia, 18 October 2014
- Round 3 Rio de Janeiro, Brazil, 15 November 2014
- Round 4 Punta del Este, Uruguay, 13 December 2014
- Round 5 Buenos Aires, Argentina, 10 January 2015
- Round 6 Los Angeles, USA, 14 February 2015
- Round 7 Miami, USA , 14 March 2015
- Round 8 Monte Carlo, Monaco, 9 May 2015
- Round 9 Berlin, Germany, 30 May 2015
- Round 10 London, UK, 27 June 2015

the Championship rules. The ten teams have been announced and the race calendar unveiled for

the inaugural competition. Drayson Racing from the UK was the first team announced, followed by China Racing of China; Andretti Autosport of the USA; Dragon Racing also from the US; e.dams of France; Super Aguri of Japan; Audi Sport ABT from Germany; Mahindra Racing of India; Virgin Racing from the UK and Venturi Grand Prix Formula E Team based in Monaco.

The races will take place on city street circuits to best showcase electric cars in their ideal environmen- city life. Each team will have two cars that will each be used for half a race to allow for high-octane racing without the need to re-charge the battery.



Amprius raises \$30M to commercialise high capacity lithium-ion batteries

alifornia-based Amprius has raised \$30M in a funding round to bring its silicon-based lithium-ion battery to commercialisation.

The money has come from private investors who have previously invested in the company including SAIF, a large Asian private equity firm. This funding round brings Amprius' total funds to \$61m. Dr. Kang Sun, CEO of Amprius said: "funding will hasten the commercialisation of our high energy and high capacity batteries and the ongoing development of siliconbased anodes, advanced cathodes, and innovative manufacturing processes."

Amprius's batteries are already being shipped in small numbers to an undisclosed Asian manufacturer for use in smartphones. •

Panasonic lithium-ion production capacity to explode on EV demand

Panasonic is planning a big increase in lithium-ion battery capacity in 2014 to cope with increased demand for hybrid and electric vehicles.

The company will add capacity at three sites in Japan. Firstly, Panasonic will add a fourth line at its Kasai plant in Hyogo prefecture, which makes prismatic lithium-ion batteries for Toyota, Ford and Audi.

Secondly, it will add a line at its Suminoe plant in Osaka, which makes cylindrical lithiumion batteries for Tesla Motors and personal computers. Thirdly, Panasonic will begin cylindrical cell production for cars at its Kaizuka plant, also in Osaka.

The ramp-up comes amid complaints from Tesla CEO Elon Musk that bottlenecks in battery supply are limiting sales of the Model S. Panasonic has been the sole battery supplier for the Model S, but Tesla is in talks with Samsung SDI of South Korea.

Panasonic and Tesla Motors have reached an agreement in which Panasonic will supply nearly 2bn cells until 2017, up from around 200m shipped since 2011. The cells will be used to power the Model S as well as Model X, a performance utility vehicle that is scheduled to go into production by the end of 2014. Panasonic says its

expansion aims would offset shrinking business in traditional batteries for cell phones and computers, which is being squeezed by low-cost rivals in China.

Panasonic officials declined to detail how much capacity it will add. Its global capacity for automotive prismatic lithium-ion batteries has surged from just 100 000 cells a month in 2010 to 2m cells a month today. This would be sufficient for approximately 28 000 vehicles per month at an average of 70 cells per vehicle.

Panasonic makes the box-shaped prismatic batteries for the Audi Q5, Toyota Prius V, Ford Fusion and C-Max hybrids, as well as for the plug-in variants of the Prius hatchback and the Ford Fusion and C-Max. It also supplies the Toyota eQ electric minicar.

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Toshiba, GNF launch energy storage battery

Multinational electricity distribution firm Gas Natural Fenosa (GNF) and Toshiba have announced a collaborative testing and verification programme for Toshiba's transportable lithium-ion battery energy storage system (BESS).

The five year demo project will be undertaken at a distribution substation in Madrid and moved to different locations in the future. It is supported by Japan's New Energy and Industrial Technology Development Organisation (NEDO), as part of its programme for 'Development of Large Scale Energy Storage System with High Safety and Cost Competitiveness.'

The aim is to see effectiveness of the BESS in contributing to peak shaving and managing electric supply at specific sites with fluctuating power demands.

In addition, management of power and voltage fluctuations caused by renewable energy sources will be evaluated. The demonstration equipment consists in a transportable BESS with 500kW output and 776kWh capacity.

Toshiba and GNF are hoping the BESS will make a worthwhile contribution to establishing metropolitan distribution networks with stable power supply even with the use of integrated renewables. •

DCB Power win IET award

Dual chemistry battery makers DCBPower Inc. won the Start-up Award at the 2013 UK Institute of Engineering and Technology Innovation Awards. The company was recognised for its battery system that comprises two separate cell chemistries which increases efficiency and utilises 100% of batteries energy thus resulting in increased driving range for EVs. •

New sales VP at Digatron

igatron has appointed Norbert Hempsch in the newly-created position of vice-president for global sales & marketing.

Hempsch will be responsible for the direction and management of the global corporate group sales and marketing activities. •

Chinese e-bikes look to lithium

hinese e-bike production tipped 35m in 2013. This included 2.6m lithium-ion battery powered bikes, an increase of 80% compared to 1.67m in 2012.

The cost of a lithium-ion e-bike battery is 1000RMB (\$160), which is double the price of a lead-acid battery. This has been an obstacle for sales in the past, however the crackdown on lead producers has given momentum to lithium-ion. •

Volvo builds battery into car body



V to integrate batteries and supercapacitors into the materials of a car so entire bodywork panels would become a battery.

Working with researchers from Imperial College London and a consortium of engineers, Volvo has developed a nanostructured lithium-ion battery surrounded by carbon fibre composite material.

Volvo is testing a prototype of the battery in its S80 gas-powered model. The integrated lithium-ion battery has replaced the regular 12V SLI battery.

It features rechargeable panels made of layered polymer-infused carbon fibre that act as the anodes and cathodes.

The carbon fibre is layered and shaped before being cured in an oven to set and harden. The supercapacitors are integrated into the component skin, which can then be used as the car's hood, roof and side door panels. In the prototype model it forms the boot lid and plenum cover. The carbon fibre energy storage sheets can store power from regenerative braking as well as mains charging.

The boot lid is a functioning electrically powered storage component and has the potential to replace the standard batteries seen in today's cars. It is lighter than a standard boot lid, saving on both volume and weight.

Volvo said the prototype featuring the energy storage plenum demonstrates that it can also replace both the rally bar, a strong structural piece that stabilises the car in the front, and the startstop battery. This would save more than 50% in weight and is powerful enough to supply energy to the car's 12V system.

It is believed that the complete substitution of an electric car's existing components with the new material could cut the overall weight by more than 15%.

Volvo did not discuss the safety implication of having the battery in the outer shell of the car. •

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Boeing Dreamliner fires – still no answers

L seems hard to believe a year has passed since the entire Boeing Dreamliner fleet was grounded following two separate fires on-board lithium-ion batteries and still the cause is not known.

The investigation is due to be completed by the end of March 2014, according to the National Transportation Safety Board.

Following extensive investigations that included dismantling and documenting both the damaged cells and control cells for comparison; CT scans were used to examine the internal configuration of the cells.

System-level testing of the battery monitoring and charging equipment on the planes. This included characterisation of the thermal and electrochemical properties of the battery and oscillatory testing. An evaluation of all related safety features was carried out; Extensive interviews were conducted with all personnel who worked on or with the battery and charging systems.

Work was undertaken in the US, Japan, France and Taiwan– as well as the NTSB working closely with the Federal Aviation Administration.

Despite this extensive work a cause has yet to be established.



In both incidents the battery located in the rear of the plane that controlled auxiliary onboard electronics caught fire. The fleet was cleared for flight after substantial casing around the battery to contain any smoke or flames was added. •



East Penn President 'Outstanding Leader'

aniel Langdon, President of East Penn has been named as 2014 Outstanding Business Leader at Northwood University's annual awards for US business men and women.

A President, Langdon is in charge of sales, marketing and the financial functions of East Penn's \$2bn lead-acid battery business.

Langdon joined East Penn

in 1986 as controller before becoming vice president of finance and chief financial officer, then finally President in 1994.

Within the wider battery community, Langdon has served as president of Battery Council International (BCI) as well sitting on the board of directors; Langdon is on the board of the Automotive Aftermarket Suppliers Association (AASA) for the North American aftermarket supply chain.

The gala award dinner will recognise eight people for business achievements in a professional or community environment.





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14 Chinese manufacturers approved to continue production by MEP

The Ministry of Environment Protection (MEP) in China has announced the second batch of lead-acid battery manufacturers and smelters that meet the environmental protection laws. The

announcement was made on 17 December 2013 after investigations and assessments carried out by the ministry.

The list of 14 companies includes 12 lead-acid battery manufacturers with



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ROCHE M'Tech - 15 Boulevard Marcelin BERTHELOT - 51100 REIMS - France Phone +33 326 078 759 - Fax +33 326 026 745 - meshmaker@roche-meshmaker.com capacities ranging from one to three million KVAh per year, and two battery smelters with capacity from 100 000 to 300 000 tons per year.

The first batch of ten approved lead-acid battery manufacturers was announced in April 2013. Smaller manufacturers have been closed down under the same rulings: 44 producers with a combined capacity close to 8m KVAh have been shut down for having 'outdated capacity'. The rulings have been imposed to allow Chinese authorities to better police the remaining manufacturers.

A Chinese television report on 11 January revealed some small factories that have not passed the environmental protection regulations continue to operate unlawfully overnight.

The 14 companies approved for continued operation are:

- Changsheng Electrics, Jiangsu Factory
- Guangzhou Fengjiang New Battery Technology Co.,Ltd
- Henan Yuguang Gold and Lead Co.,Ltd
- Jiangsu Shuangdeng Group Co.,Ltd
- Jiangsu Yonder Power Industry Co.,Ltd
- Narada Power Source Co., Ltd
- New Chunxing Resource Recycling Group
- Shandong Chilwee Power Limited Corporation
- Shanxi Jitianli Technology Co.,Ltd
- Shenzhen Center Industry Co.,Ltd
- Shenzhen Center Power Tech Co., Ltd
- Tangshan Hongwen Battery Co.,Ltd
- Yangzhou Apollo Battery Co. Ltd
- Zhangjiakou POWSEA New Energy Technology Co., Ltd 🗘

Water Gremlin opens factory in Zhejiang

ater Gremlin Non-Ferrous Co has opened a factory in Zhejiang, China to manufacture terminals for lead-acid batteries for the Asian market. 🗘

Harvard creates low-cost organic flow battery

A research team from Harvard University is developing a gridscale flow battery using quinones as the electrolyte.

The metal-free flow battery uses carbon-based quinones, which are naturally abundant, inexpensive, small organic molecules that store energy in plants and animals, for the electrolyte.



More than 10 000 quinone molecules were screened to find the ideal candidate for the battery.

The flow battery works by storing energy in the quinones in external tanks. These tanks dictate the capacity of the battery– the amount of energy stored is only limited by the size of the tanks, this means large amounts of energy could be stored at lower cost than in traditional batteries.

The team claims the battery already performs as well as the most commercially advanced vanadium flow batteries but with far lower-cost components and chemicals.

Roy Gordon, professor of chemistry and materials science, one of the professors leading the research said: "With organic molecules, we introduce a vast new set of possibilities. Some of them will be terrible and some will be really good. With these quinones we have the first ones that look really good."

Quinones are found abundantly in crude oil and vegetation. The molecule used in the Harvard flow battery is very similar to that found in rhubarb.

Stored in tanks, the quinones are dissolved in water to prevent combustion. For commercial or home use, a tank could be stored in a basement or external storage tank with sufficient energy stored for the needs of the attached generating system. The progression from laboratory testing to commercial scale will require further work. "So far, we've seen no sign of degradation after more than 100 cycles, but commercial applications require thousands of cycles," said Michael Aziz, professor of materials and energy technology. "I think the chemistry we have right now might be the best that's out there for stationary storage and quite possibly cheap enough to make it in the marketplace," he added.

The team anticipates being able to deploy demonstration versions of the battery in a container on a trailer within the next few years. •

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Exide and Quemetco smelters ordered to clean up act

wo lead-acid battery recyclers in the US have been ordered to clean up emissions from their plants or be prepared to face shutdowns.

Quemetco and Exide Technologies, both based in California, have been told by the South Coast Air Quality Management District (SCAQMD) board to reduce emissions of contaminants, specifically lead, arsenic, benzene and 1,3-butadiene over the coming year.

The demand follows a report in December 2013 from the Californian Department of Toxic and Substances Control that found elevated lead levels in soil around Exide's plant at Vernon that posed "an immediate threat to human health".

Exide has come under

scrutiny in the past 12 months following a report showing arsenic emissions from its Vernon smelter spiked the cancer risk in the area.

The Vernon plant processes around 25 000 batteries eachday, averaging eight million over a year. Following scrutiny the company worked to reduce its lead emissions by cutting back on lead smelting activities. The plant manager, John Hogarth, is confident the company can meet the arsenic emission reductions of 95% but does not support the SCAQMD intention to lower lead emission rates to below o.o2kg/h in the future.

Quemetco is confident its own lead emissions are already below the intended lower rate of emission. However, its arsenic, benzene and 1,3-butadiene emissions are

Hybrid anode holds promise for lithium-sulphur

A hybrid anode of lithium and graphite has significantly extended the lifecycle of lithium-sulphur batteries at Pacific Northwestern National Laboratory (PNNL), US.

Lithium-sulphur holds the promise of four times greater energy density than lithiumion but are prone to short life due to sulfation.

Research into lithiumsulphur has previously focused on overcoming sulfation by stopping the sulphur leaking from the cathode. However, the team at PNNL instead looked at ways to protect the anode with a shielding graphite layer.

This layer redirects the sulphur from the anode to stop it forming a damaging surface layer. The research team claims the hybrid anode increases the cyclelife to four times that of a lithium-sulphur battery with a standard anode— tipping 400 chargedischarge cycles.

The graphite layer does, however, decrease energy density by 11%.

Further tests are being undertaken to test the battery's effectiveness in real-world applications. • currently three times that of the regulation limit. The SCAQMD has estimated the cost to the plants will be around \$1.8m a year to adhere to the emission reduction regulations. •



Aquion secures \$55m for sodium-ion battery

quion Energy, the Pennsylvania based start-up working to commercialise an aqueous hybrid-ion battery, has secured \$55m of capital investment for manufacturing its grid-scale product.

The investment includes \$35m from a funding round closed in April 2013 and a subsequent \$20m, which brings the total investment to over \$100m.

Aquion's battery is composed of an aqueous water-based sodium sulphate electrolyte, a cathode of manganese oxide, an anode of activated carbon and a cotton



separator.

Investors, including Bill Gates, have enabled the company to develop its product to a stage that Aquion claims can deliver 85% energy efficiency, a 5000 cycle lifetime and a charge-discharge capacity suited to grid cycle usage, all for \$250 per kWh.

Aquion will use the investment money to ramp up production at its plant in Pennsylvania ready for its first commercial delivery later in the year.

Aquion's batteries are scaleable based on a 1.5 kWh S10 battery stack that are already in use in off-grid

> and grid-tied systems around the world.

The company has a deal with Siemens to supply batteries for grid-scale testing to the German company. •

Government urged to do more to recycle batteries in China

The Chinese government should be doing more to regulate the recycling of lead-acid batteries, according to a report from the Ministry of Environmental Protection (MEP) in China.

The Policy Research Centre for Environment and Economy, a think tank affiliated to the MEP, has drawn up the report recommending the government should improve policies and formulate measures to better regulate the network for recycling lead-acid storage batteries.

One of the policy writers, Shen Xiaoyue, said: "China is the biggest producer, consumer and exporter of lead-acid storage batteries in the world. More than 2.6m metric tons of waste lead-acid storage batteries are generated in China every year, but less than 30% are reclaimed and processed under official standards."

In contrast to developed countries where lead-acid battery reclamation is around 95%, China has a long way to catch up.

Almost 900 000 tons of waste from lead-acid plants went untreated into the air, water and soil between 2008 and 2012, according to the China Battery Industry Association. Although regulations are in place for recycling, storage and disposal of lead-acid storage batteries, enforcement has not been stringent enough, the MEP report said.

Between 2007 and 2009 more than 6 000 children were reported to be suffering from excessive blood lead levels across the country. This lead to mass shut down of lead-acid battery manufacturing sites until regulations could be imposed.

There are 40 companies qualified to handle hazardous waste in the country, but only five are authorised to transport and dispose of used lead-acid batteries. This has lead to a rise in illegal dealers disposing of waste batteries. These unregulated dealers are far cheaper than authorised recyclers, which results in more customers opting for the lower cost option.

Beijing's only authorised recycling centre Beijing Ecoisland Science and Technology Co., can handle 20 000 tons of spent batteries each year but is currently not processing more than 7 000. As a business, collecting and recycling batteries is not profitable in China.

In 2013 Ministers set a target of 90% recycling rate by 2015. 😌





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| Model : | COS-32/62 |
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| Application: | To weld the group of plates |
| Production Capacity: | 80-90pcs /hour (calculated by 70AH Car battery) |
| Operator Required: | Two operators (One is for loading, the other one is for unloading) Same Production Capacity Operator Required for Group Burning: Four Operators |
| Production flow: | Loading the plate groups and Lug Alignment—Lug Brushing, fluxing and Tinning—Cast on Strap –Unloading |
| Power Consumption: | AC38V/220V, 50HZ, 46KW |
| Air Consumption: | 0.55MPa 0.2m³/min |
| Water Consumption: | 20L/min, 0.2Mpa |
| Machine Weigh: | 600Kg |
| Machine Dimension: | 3800×3200×2000mm (not included the foundation bolt and dust collection hood) |
| Work Position: | four work position |

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Specifications:

| Model : | SEPG-32/62 |
|----------------------|---|
| Application: | Realization of production of single plate to the group of plates |
| Production Capacity: | 120pcs/min |
| Production flow: | Loading the plate in the first work position—Enveloping—Loading the plate in the second position—Loading the plate in the third work position—Plate groups alignment-Collection |
| Power Consumption: | 3P AC 380V 50HZ |
| Air Consumption: | 0.55MPa 0.2m³/min |
| Machine Weigh: | 4000Kg |
| Feature: | Can wrap both positive and negative plate, Check the plate quantity more or less, suitable for different type of plate, with safety switch. |
| Machine Dimension: | 10900mm × 4500mm × 2800mm |



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REDT among winners of UK energy storage competition funding

REDT has won £3.6m (\$6m) funding under the UK's Department of Energy and Climate Change 'Energy Storage Technology Demonstration' competition to develop a 1.26 MWh flow battery project.

The Irish-based firm has developed a vanadium redox flow battery (VRFB) to store energy generated by wind turbines. The company is ready to design, build and demonstrate a system for a project in the Scottish island of Gigha, situated a few miles off the Kintyre peninsula, which has limited connection to the mainland via an ageing subsea cable.

Project partners include Scottish and Southern Energy– Power Distribution (SSE), EA Technology Ltd., Community Energy Scotland (CES) and Gigha Green Power Ltd. (GGPL).

Generation and distribution issues to be addressed on Gigha include storage of 'wrong time' wind energy produced by the established wind farm on the island and dispatch at peak rates, peak shaving and power regulation; deferral of capital upgrades of over-utilised transmission assets; potential standby power for the island during network faults or power outages; and enabling a minimum 20% increase in wind and solar generation with associated additional income for the island.

Meanwhile, London-based Moixa Technology was awarded £1.5m (\$2.5m) to demonstrate its small domestic battery storage units that store power for use at peak demand times. The lithium iron phosphate system shifts DC loads to the battery, which can be charged at low tariff times, to reduce peak grid demand and reduce energy bills.

Moixa will use their funding from DECC to install and demonstrate their storage units in about 300 homes across the UK.

The competition aims to encourage the development of innovative, pre-commercial energy storage technologies that can address grid-scale storage and balancing needs in the UK electricity network.

At the time of going to press, cryogenic energy storage Highview Power Systems was expected to secure a portion of the £20m (\$33m) total funding pot. The funding would be to develop a commercial scale, 6 MW/30 MWh liquid air energy storage demonstration project in England's Isle of Grain.

Three more companies won a share of £0.9m (\$1.5m) to continue research and material development to improve energy storage systems for the UK electricity networks.

Kiwa GASTEC at CRE was awarded £0.4m (\$0.7m) to investigate safety issues surrounding the use of hydrogen for energy storage; Sharp Laboratories received £0.4m (\$0.7m) for its work on residential and community battery storage systems; and EA Technology Ltd received £0.1m (\$0.16m) to develop a good practice guide on electrical energy storage for use in and with UK electricity networks. •

Trojan Battery includes carbon additives as standard for industrial batteries

rojan Battery has become the first lead-acid battery producer to use Smart Carbon as a standard additive in its industrial and premium flooded battery lines. Smart Carbon is Trojan's own proprietary formula that provides improved battery performance in partial state of charge applications (PSoC).

Trojan's engineering team has developed the Smart Carbon formula to boost battery performance and extend lifecycle in renewable energy, telecom and inverter backup systems applications which regularly operate in an under charged state. Trojan said carbon additives help prolong battery life are important in these fields because the battery is one of the most expensive components of the systems.

"Trojan Battery is the first manufacturer to introduce a carbon additive as a standard feature in its deep cycle flooded batteries used in renewable energy, inverter backup and telecom applications. Trojan's engineering team has spent more than five years in research and development experimenting with many types of carbon to ensure the right formula to successfully address PSoC," said Bryan Godber, senior vice president of global market development at Trojan Battery.

Although most R&D into carbon additives has focused on their uses in start-stop hybrid automotive applications, Trojan has chosen to concentrate on deep-cycle flooded batteries for stationary applications because this technology is widely used in off-grid and grid stabling applications.

Trojan believes the benefits will be felt in areas where batteries are heavily relied upon for grid stabling such as parts of the world prone to power outages throughout the day. In these scenarios deep-cycle batteries are under-charged on a regular basis resulting in diminished life expectancy and higher total cost of ownership. \bigcirc

See page 35 for BEST's 'Dummy's Guide to Carbon Additives'

Amer-Sil and Vidyut Insulation form Indian joint venture

Mer-Sil, a maker of separators and gauntlets for industrial batteries, and Vidyut Insulation Pvt Ltd, an Indian producer of woven tubular bags, have formed a joint venture.

Amer-Sil Vidyut Microporous Membranes Pvt, Ltd. will establish two production sites in India to increase the production of woven tubular bags, introduce non-woven gauntlet technology and produce industrial battery separators.

The current managing director of Vidyut, Rohit Kauntia, will be responsible for this newly formed company. The headquarters of Amer-Sil Vidyut Microporous Membranes Pvt, will be located in Hyderabad.

In an emailed statement the companies said: "Amer-Sil Vidyut will provide superior quality and service and a wider product range, at competitive prices, for tubular bags.

"The new JV will also offer local supply of superior separators for inverters, gel and other stationary batteries. This will contribute to the continuous improvements in life, performance and cost that are increasingly required for the various battery types." C





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besttechreview 35

The dummy's guide to carbon additives for lead-acid batteries

Adding carbon is the new lease of life for lead-acid batteries. Light, abundant and relatively inexpensive, this material offers unique benefits to the battery electrodes and to the construction– making it better and stronger than ever before. ALABC programme manager Boris Monahov takes a comprehensive overview of the subject so you can make the best lead-acid batteries yet.

arbon is the sixth major element used in lead-acid batteries. The electrolyte of lead-acid batteries attacks most materials except steel, some glasses and some polymers. But carbon is considered chemically stable in sulphuric acid solution. That is why carbon black is one of the few 'foreign' materials added to the negative active mass (NAM) along with barium sulphate, glass or polymer flock, and lignosulphonates.

Since it is electronically conductive it helps to recharge deeply discharged negative plates by building conductive paths through the active mass. Why have so many battery researchers and manufacturers considered the use of higher concentrations of carbon in lead-acid battery negative plates as a way to improve their quality– in so far that some are speaking about 'a new generation' of lead-carbon batteries? Can we think "the more carbon added – the stronger the battery"?

No, carbon is good for the battery only in certain concentrations. *Maybe a new form of carbon has been invented, in addition to nano-sized carbon particles and*



carbon nanotubes (CNT)? Actually no, the currently available forms are working pretty well. Then, why are the 'high carbon' carbon batteries so much better than the 'conventional' ones?

Why add carbon? It's simple!

Many studies have shown that, using carbon in the negative plate in various ways— as an additive to the negative paste, or as part of the negative plate, enhances the performance of the battery. Carbon helps for easier and more complete recharge, especially by high current pulses. On discharge the battery provides more power, and more energy. Cycle life is also increased dramatically.

'Carbon added' batteries perform extremely well in the hottest applications like hybrid electric vehicles (HEV), renewable energy storage and grid quality support systems.

Service life is as long as other advanced batteries, and they are able to transfer much larger amounts of energy during their entire service life [1]. Carbon influences the rate of crystal growth in the battery. Lead sulphate crystal growth and



recrystallisation is slowed down to such an extent that one of the major battery failure modes caused by negative plate sulfation is almost completely suppressed **(Figure 1)**. Lead-carbon (LC) batteries don't have the issues observed with 'regular' lead-acid batteries and can be used as a power source in start-stop, mild and micro HEVs and in energy storage systems.

Finally, carbon is inexpensive and easy to use without serious changes in production technology, clean and safe. It improves lead-acid batteries but keeps their cost low.

Lead-acid performs better, last longer with carbon and the batteries stay cheap!



ALABC experience with carbon in the negative active mass (NAM)

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 a. Carbon changes the microstructure of the NAM by reducing the size of the PbSO₄ and Pb crystals, increases the specific surface area and provides extra porosity to the NAM.

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Fig. 1. Voltage vs. time profiles on HRPSoC cycling of: a) a "regular" battery; b) an Ultrabattery (ALABC project DP 1.8, 2010).

- b. Carbon strongly increases the charge acceptance of the negative plate. The reaction rate difference between the charge and the discharge reactions is reduced— no lead sulphate accumulates on cycling. The dynamic charge acceptance of carbon-added batteries is much better than of 'regular' ones.
- c. Since negative plate sulfation is suppressed, cells with added carbon have much longer cycle life at high rate partial state of charge (PSoC) operation— ideal for hybrid electric vehicles, renewable energy storage systems, grid quality and demand control in decentralised and smart grids.
- d. The use of carbon needs to be well understood and controlled. If not carefully selected, and if not used in the best way, carbon can reduce the low rate

discharge capacity or the cold cranking performance of the battery. It can also cause higher water loss.

e. Finally, the improvement of the negative active mass makes demands on the other active materials in the cell. The positive active mass must be able to withstand tens of thousands of cycles and provide excellent energy and power. The amount of sulphuric acid solution needs to be increased as well.



Which type of carbon to use, and why?

Carbon exists in various allotropic forms with different microstructure and properties. The carbon atoms in some are ordered (diamond and graphite), in others only partially or not at all (carbon black, activated carbon).

New types of carbon have been created, in laboratories, which





Fig. 2. SEM images of negative active material (NAM) after 100,000 HRPSoC cycles (magnification 3,000x, 20µm scale bar): a) no Carbon additives; b) 1% graphite plus 1% carbon black.

have perfect but differently ordered microstructures and unique new properties. These are fullerenes, carbon nano foam and hydrogel, carbon foam and glassy carbon, activated carbons with various functional groups bonded to their surface. While graphite, carbon black and activated carbon are already used, most of the new materials are still under test.

Carbon is used in lead-acid batteries in four ways:

- a. Replacing the entire negative plate with carbon of high capacitance (PbC battery, Axion Power);
- **b.** Replacing part of the negative plate with an ultracapacitive carbon plate, to combine a battery and an ultracapacitor in a single device (Ultrabattery, CSIRO, Furukawa, East Penn);
- **c.** Replacing the lead grid (or part of it) with a solid 3D porous carbon structure:
 - reticulated vitreous carbon (Power Technology)
 - carbon foam (Firefly Energy)


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d. Adding carbon powder or organic additives to the NAM.



Types of carbon products added to lead-acid batteries

- 1. Solid 3D porous materials with specific macrostructure and open pores. These are designed to replace, fully or partially, the metallic lead grid, or to support it. They have a homogeneous microstructure of branches ('struts'). The integrity of the material do not change over battery life, so these 3D materials play the role of a NAM exoskeleton. The following 3D carbon structures include:
 - a. Reticulated vitreous carbon. The struts of the 3D networklike structure are built of amorphous carbon and have a smooth surface of rather low surface area. Because of the relatively low intrinsic conductivity of amorphous carbon, lead is electrodeposited at the carbon surface. A good conducting grid is formed and the NAM stays in good contact to the 3D structure. RVC can be produced from various precursors. It seems to be pricy compared to lead, but cost will fall if large scale production begins.
 - b. Graphitic or carbon foam (GF

or CF) looks similar to RVC but the struts form cell-like pores of about 0.5 mm in diameter where portions of NAM can be placed. Graphitic foam has higher electronic conductivity than RVC, and can fully or partially replace the lead grid. It is not necessary to electrodeposit lead on it, which makes this technology



simpler and cheaper than the RVC. The cost of carbon foam can be substantially reduced. Batteries with carbon foam negative plates have been developed first by Firefly Energy Inc. and showed exceptional cycle life (1400 deep cycles) and high NAM utilisation (70%). Electrodes and cells with GF have been studied also by Oakridge National Laboratory in the USA, by the South Normal University in China, and by TAFE Battery Company in Iran. Carbon foam is a good grid material for both negative and positive plates.

c. Carbon honeycomb (CH). This material has been developed by CEA-INES, France. It is produced by carbonising low cost, paper based precursors. The amorphous carbon matrix has open macro pores of 0.5–1mm diameter, ordered and structured like a honeycomb. After electroplating with lead, the honeycomb plate is pasted like a regular negative plate. The technology works well in both positive and negative plates.

Batteries with 3D carbon grid replacing structures offer higher utilisation of the active materials and thus higher specific energy, high specific power, plus excellent cycle life. The weight of the negative grids is about 10% of the entire battery weight. If they are replaced by carbon, and the NAM is better utilised by 10-15%, the effect of carbon to the battery can provide 5-10% more specific energy and power without changing paste technology. The combined benefit of solid 3D carbon structures can be as high as 15-25% higher energy/power. A transition from 35-40 Wh/kg to

40-55 Wh/kg has the potential to change the preferences of automotive engineers for powering hybrid electric vehicles.

- 2. Solid, non-homogeneous 3D macrostructures of high electron conductivity. Composites and engineered carbon materials of high conductivity and good contact to the NAM offer another way to replace the lead grid. These materials allow also replacing the top lead by light carbon-based materials. The gain in weight could reach values of about 10-15%. These materials can offer a new way to further increase the specific energy up to 60-65 Wh/kg without changing the paste.
- 3. Carbon / graphite fibres with solid 3D macrostructure. They are added in a same manner and for the same purpose as flock or glass micro fibres are added to the NAM.
- 4. Carbon powder additives to the NAM without macrostructure. The ALABC has revealed the huge potential benefits for the battery of adding carbon to the NAM. The variety of both the carbon powders and the methods for adding them to the battery, makes it available for every battery producer. This is why added carbon powders are important for the industry. Adding carbon in concentrations between 0.5 wt. % and 4 wt. % (vs. leady oxide weight) is the most affordable and efficient way for massive battery improvement in HEV and in renewable energy and grid support storage systems.
- 5. Nano-sized carbon particle additives without own macrostructure. Several types of carbon with specifically ordered

atoms have been developed, like fullerenes, carbon nano tubes (CNT), graphene, carbon nano foam. These materials have unique properties and show highly intriguing test results in lead-acid batteries. Recent studies have found two outstanding CNT applications: as an active mass additive; and as part of carbon grids. It seems that the high initial cost can drop to affordable levels. Graphene has also offered substantial improvements of NAM performance.

6. Organic compounds (solid powders, liquids). Some crystalline or liquid organic compounds added to the

compounds, added to the negative active mass or to the electrolyte, can influence the crystal growth rate of lead and lead sulphate. The molecules of some organic compounds (for instance lignosulphonates) have strong specific adsorption to the surface of Pb or PbSO₄ crystals in sulphuric acid. Their accumulation at the surface changes the conditions for nucleation and crystal growth of these phases. In many cases the growth of PbSO₄ crystals, or their re-crystallisation, is slowed down. This is for instance the case with polyaspartic acid, studied in details at the Bulgarian Academy of Sciences by the team of D. Pavlov [2]. Fine and highly active PbSO₄ crystals of high activity are formed, which don't agglomerate and re-crystalise.

Many organic additives are offered as 'de-sulfating' agents which can be added to the electrolyte or to the negative paste. Their influence on sulfation, hydrogen evolution, battery performance and durability has been studied by different authors: expander compounds with large organic molecules (works of D. Pavlov, B. Myrvold, P. Spinelli, D. Boden, T. McNally, etc.); liquid polymers (works of D. Pavlov et al.), light organic compounds (B. Monahov, K. Kelley, M. Alkhateeb); phenolic compounds (Al. Russin); "batcure" desulfation solution (S. Pandya); polyvinyl alcohol and acrylic polymers (Kozava); polymer gels like polyacrylamid (W. Siridetpan) and the synthetic polymer "Electrogel" (S. Pandya).

How carbon works Patrick Moseley [3] has summarised eight key mechanisms which, solely but more likely in combination with each other, determine the effect of carbon. In a dual electrode model developed by Firefly Energy [4] the electrochemical activity of locally formed carbon electrodes is considered along with the electrochemical processes taking place in the Pb/PbSO₄ NAM.

The detailed physic-chemical and electrochemical model of carbon containing NAM, developed by D. Pavlov et al. between 2007 and 2009, considers the physical and electrochemical properties of carbon as a new electrode and the joint operation of two electrodes— lead/ lead sulphate and carbon ones— in the areas where the capacity bearing reaction takes place.

However, battery engineers are still missing a universal, quantitative model of the influence of carbon, which could allow them to predict and engineer the performance of the advanced lead-carbon cells.



What happens with the carbon powder in the negative plate?

Carbon powder is added during paste mixing to the negative paste. It gets connected to the negative active mass and remains there



through the life of the battery. The following steps are important for achieving a stable and better performing carbon added NAM:

- a. Carbon suspension. When the carbon powder comes in contact with the liquid paste components, the particles get wet by the liquid and form a suspension. The carbon surface is covered by a liquid film. The surface tension and the wetting angle at the solid/ liquid interface depend on carbon type, surface chemistry and nature of the liquid. The consistency of the slurry changes strongly due to the interaction of the light carbon particles with the liquid around, this is why it is important how carbon is mixed - with water or with electrolyte. Some liquid gets bonded to the carbon particles. When they have high surface area, this effect is strong and the viscosity increases rapidly. Extra liquid is needed for maintaining the consistency of the paste. In some cases pre-soaking the carbon in a good wetting liquid helps for easier paste mixing.
- **b.** Once the carbon particles are mixed into the paste they will remain there, unless the amount exceeds a certain threshold. On drying pasted plates, some carbon particles remain covered by basic lead sulphate, while others get partially dry. If the surface of these particles is plumbophobic, no lead compounds will be formed there. Cavities and pores will be formed. When the cell is filled with electrolyte, these pores form locally microscopic containers for extra electrolyte. The large carbon particles which are partially bound to the

NAM and partially exposed to the electrolyte form a number of carbon micro electrodes which will operate in parallel to the lead ones.

- **c.** Since lead ions are heavy, and the mobility of sulphate ions is limited, the microstructure of freshly formed NAM will be similar to this of the dry paste. Some carbon particles remain imbedded in the microstructure of the lead skeleton. They decrease its conductivity but do not affect the surface area. Most of the large particles remain partially covered by NAM, partially surrounded by electrolyte. They increase the surface area. New interfaces are formed in carbon added NAM: carbon/electrolyte, carbon/ lead and carbon/lead sulphate, as well as their combinations. The electrochemical processes in these interfaces proceed in a different way than in 'regular' paste.
- **d.** On cycling, because of the low mobility of surrounding lead and sulphate ions, the location of the carbon particles will not change substantially.
- e. Due to the increased surface area of carbon-added NAM more hydrogen is evolved at the end of charge. Some hydrogen is also evolved on the carbon surface exposed to the electrolyte. This requires a careful selection of the amount and type of carbon in order to prevent increased water loss.



Future trends of using carbon in lead-acid batteries

Carbon is expected to further the performance of lead-acid batteries. The following research trends can be highlighted:



- Development of carbon additives with engineered properties, which can totally block negative plate sulfation and increase the utilisation the negative active material yielding even higher specific energy and specific powder.
- 2. Finding ways for using the beneficial effect of carbon on the positive active mass (longer cycle life).
- **3.** Development of carbon nano tubes specifically designed to improve LAB (massive improvement in crystallisation control and cycle life).
- **4.** Development of highly efficient organic additives to the active masses and to the electrolyte.
- 5. Replacing lead in grids and top lead with conductive carbon structures (up to 25% weight reduction, i.e. Wh/kg and W/kg improvement).

Carbon is not only the future of lead-acid batteries but probably its saviour. A variety of carbon additives are already available, but the way they work is only partially understood. Filling this gap is the biggest challenge for lead-acid batteries in their history. For the battery industry, developing the most efficient carbon additives and learning how to use them in the best way is the key for keeping its leading position on all battery markets and remaining the best and preferred power source. •

The full version of this article appears in the digital edition of BEST Winter 2014.

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Producers of carbon powder additives for lead-acid batteries

ALABC members:

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Carbon additives: Add a little something

Carbon additives give lead-acid batteries a bit more oomph. But with so many options out there, what is the best for your lead-acid battery design? Ruth Williams talks to the producers to find out.

In the face of newer chemistry options, pro-lead lobbyists make the arguments that lead is familiar, reliable and cheap versus lithium-ion and the advanced battery posse. As cars change to reduce fuel usage and accommodate carbon emission rules, the lead-acid chemistry needs to adapt quickly to keep its stronghold in automotive batteries.

Lead-acid batteries can have a facelift by way of carbon additives to give it a second wind as lithium-ion encroaches on its ground. Chemical additives have been used in batteries since the 1950s with varying degrees of success to combat sulphation. The traditionally used expanders have been a blend of barium sulphate, lignosulfonate, and carbon.

Out of the classic blend, carbon has been the 'redheaded stepchild'— overlooked in studies that focussed on lignosulphonate. But now carbon is receiving plenty of attention having come to the forefront of thought as partial state of charge applications became more prominent.

Most people are aware of the partial state of charge model for lead-acid operation to accept a charge at any time in any state and use that energy on demand, such as in stop-start applications. In Europe the majority of new cars are built with stop-start engines. Indeed, Ford says it will



aggressively push the technology in its models saying that 70% of its cars will have at least this level of hybridisation by 2017.

Energy conservation and the need to reduce carbon emissions feeds the second market for partial state of charge applications: Stationary batteries for use with renewable energy supplies. The stationary battery, just as the automotive battery for stop-start, needs to accept charge when energy is generated from sun or wind and deliver that energy on demand regardless of the state of charge.

The biggest problem batteries face regarding partial state of charge is sulphation. This is defined as kinetic irreversibility in formation/dissolution of lead sulphate (PbSO4) and consequently accumulation of PbSO4 in battery electrodes that leads to reduced battery cycle life. This means batteries fail because the negative active material became covered in a dense layer that builds up and acts as an insulator stopping the battery from accepting or releasing charge.

As part of a fundamental research programme undertaken in 2010 by the Advanced Lead-Acid Battery Consortium (ALABC), along with its members from the industry, the loading levels of expanders were measured to see the effect on the negative active material. In a traditional expander mix around



o.1–o.2% of carbon was added to the active material, which did nothing to prevent sulphation.

However, adding 1 - 3% of carbon to the active material created a conductive carbon network within the sulphate layer that an electrical charge could travel through to re-establish a route for the electrical current to get through. The research showed carbon additives resulted in significant improvements in cycleability, charge acceptance and reducing sulphation to the negative plate.

This has not entirely translated well into practice because incorporating the carbon additives effectively into the negative plate has proved challenging. The higher loading of carbon additives can cause difficulties in the paste formulation and pasting because it requires more water. This can lead to low paste density and poor mechanical integrity of the electrodes. So working with the right amount of additive is essential.

As an upshot of the studies, companies have begun using conductive carbons as additives that can easily be incorporated into the paste formulation and do not affect the integrity of the electrodes. Continued studies by ALABC have shown that activated carbon performs much better than graphite.

| WHICH? Additives | ΑυτοΜά | DTIVE | INDUSTRIAL | | | |
|--------------------------------|----------------------------|--------------|----------------------|--------------|--|--|
| Manufacturer Additive name | micro hybrid stop-start | SLI | traction | stationary | | |
| HAMMOND | | | | | | |
| K2 Peak Endurance | | | | | | |
| K2 Peak Capacity | × | | | | | |
| K2 Peak Stop-start | v | | | | | |
| Over 100 expander formulations | | v | v | v | | |
| Cabot | | | | | | |
| PBX09 | \checkmark | \checkmark | \checkmark | \checkmark | | |
| PBX51 | v | | | | | |
| PBX55 | | \checkmark | \checkmark | \checkmark | | |
| PBX135 | \checkmark | \checkmark | \checkmark | \checkmark | | |
| PENOX | | | | | | |
| PE100 | | v | | | | |
| PE200 | | \checkmark | | V | | |
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| 2939APH | \checkmark | \checkmark | \checkmark | \checkmark | | |
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| JEV Series | | | | | | |
| JSP Series | | | | V | | |
| TIMCAL | | | | | | |
| ENSACO/Super P | × | \checkmark | \checkmark | \checkmark | | |
| TIMREX CyPbrid | | \checkmark | × | V | | |
| TIMREX Expanded Graphite | ~ | v | \checkmark | \checkmark | | |

Activated carbon has larger particles than graphite and forms a wire-like structure in the active material, acting like an addition to the grid structure to increase conductivity in the paste. It also does not impact the active material or impact voltage shifts in the way graphite does, which leads to unwanted water losses.

Following the ALABC study, additives and expander companies began to work on blending different ratios of carbon to best suit different lead-acid battery applications. High structured carbons with high conductivity have been found to be very beneficial; these can be blended with graphites with a high proportion of carbon blacks together with other materials to create mixes for partial state of charge applications.

So what is available to better your battery?

Hammond Expanders, part of the Hammond Group, was heavily involved in the ALABC study programme and says it has opened up an avenue to focus their own research.

Hammond carries out its own research and development: "We decided two years ago to invest in in-house capability," says Achim Lulsdorf, VP of product development at Hammond Expanders. "We also participate in industry studies but we wanted to carry out independent research also. We have invested in people and lab capabilities, we are expanding laboratory and testing capabilities."

"We found early on the key to a good expander is the interaction of the lignosulphonates and the carbons. I really believe that most of what I have seen has been focused on isolating the effects of the components, I believe Hammond is among the first to methodically study the interactions. We believe the



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interactions are the key."

The result of this methodical working is the K2 line and consists of three expander blends for micro hybrid stop-start vehicle batteries: Endurance, Capacity and Stop-Start.

The blends give a range of performance enhancements depending on specific needs, but improving one aspect of performance can be detrimental to others. Lulsdorf says they recommend blends based on the exact technical specifications a manufacturer has to fulfil.

The K2 Endurance is engineered to give the maximum cycling performance for partial state of charge applications, it contains high levels of advanced carbons and graphites.

The K2 Capacity is designed for manufacturers that need a balance between the partial-state of charge performance, but still need high levels of capacity performance and cold cranking ability. The third product is the K2 Stop-Start. It mainly focuses on providing good capacity and cold crank performance, while still assuring reasonable PSoC behaviour.

Cabot Corporation, whose battery additive department is based in New Mexico, has designed a range of carbon additives for lead-acid batteries called PBX. They have varied properties to suit the needs of different applications. They are suitable for use in VRLA and flooded advanced batteries, as well as in applications that need higher levels of charge acceptance.

The first, called PBX09, aims to balance high charge acceptance with improved cycle life. It is suited to most types of VRLA and flooded batteries for applications including stop-start, telecoms, motive power and e-bikes.

The second called PBX51 is aimed at the micro-hybrid and market where dynamic charge acceptance





Courtesy of Hammond Expanders

Hybrid pulse power characterisation test results comparing a standard SLI expander formulation with the K2 Peak Capacity and Endurance products. The shaded area shows the state of charge level a battery should perform in for micro-hybrid applications. The diamonds represent points at which the test cells' charge and discharge power levels are equal.

A suitable expander for the micro-hybrid application will enable the battery to perform at high levels of SoC (>80%) with high charge and discharge power. The K2 expanders fit this requirement.

is the primary feature of the battery. Cabot recommends loading 0.25 – 1% to the negative plate slurry. Higher loading requires additional engineering to redress water loss and cold crank performance.

Cabot claims nearly double the dynamic charge acceptance and improves cycle life ten times, when used at 1%. Miki Oljaca, R&D manager of energy materials for Cabot Corporation, explains this marked enhancement: "The reason for this improvement is the introduction of additional conductive surface area to the negative electrode which enables high charge currents without polarisation of the negative electrode, therefore increasing cycle life."

PBX55 is said to improve cycle life for flooded batteries that require minimal charge acceptance such as stop-start capabilities without regenerative braking in smaller vehicles. The fourth blend is PBX135, which is a multipurpose additive that gives a balance between improved cycle life and dynamic charge acceptance.

This is designed for use in flooded batteries in stop-start and motive power applications. Cabot designed its PBX carbon additives to be able to easily incorporated into the negative paste formulation, requiring less water to be added, as well as providing higher paste density and good integrity of the negative electrodes.

The long-established multinational player **Penox**, whose additive division is based Germany, has focussed on keeping high porosity of the active materials, especially on the negative plate.

Ian Klein, R&D manager at Penox, says focusing on porosity helps to overcome sulphation: "We think that with bigger pores you have a better possibility to transport out of the pores when you charge a battery with a high current."

Working to this idea, Penox has developed three types of expander blends containing carbon additives. The first is PE100, which is used for standard SLI batteries. It is

made of a blend of the three classic expander components with a higher proportion of carbon black.

The second blend is called PE200. It is a dedicated blend for emergency starter batteries (ESB) and AGM battery applications, as well as light traction batteries. The PE200 contains a different type of barium sulphate to support the evolution of bigger pores. It also contains a high proportion of carbon black, some of which can be substituted for graphite or activated carbon.

The third type is PE300, which is for industrial batteries only. This contains a smaller amount of carbon black and highest ratio of barium sulphate. PE300 is suitable for applications that do not have specific charge acceptance issues but still benefit from carbon in the expander mix.

"At Penox we are delivering expander mixes with a different view to the function of the single materials," says Klein. "We think it is very important to keep high porosity, so we increase the internal conductivity of the paste but it is better to increase the porosity of the active materials, especially on the negative plate."

The additive is added to the negative active material to act like a seed at the point sulphation begins, i.e. during discharge. The larger the seeds, the larger the pores to allow acid flow and prevent sulphation.

Following testing Penox has seen its expander mix can increase charge acceptance by more than 20% for high current applications. The company has a new range in development that will be unveiled at the European Lead-acid Battery Conference in Edinburgh this September.

TIMCAL Graphite & Carbon, a Swiss manufacturer of carbon and graphite additives, has a range of carbon blacks and graphite additives on the market: ENSACO Conductive Carbon Black and Super P Conductive Carbon Black; TIMREX expanded graphite, and the recently launched TIMREX CyPbrid material family. This carbon hybrid material was specifically developed and combines the key properties of carbon black and graphite while addressing processing requirements and avoiding blends of carbon materials.

Thomas Hucke, head of R&D for electrochemical applications at TIMCAL says: "TIMREX CyPbrid exhibits an easy handling and processing in the electrode pasting process and has a good affinity to lead for efficient lead plating and incorporation of the carbon into the negative electrode structure. The key attribute of this material family is the carbon morphology which in terms of battery performance allows a scalable charge acceptance while at the same time stable cycling at high rate microcycle operations at partial state of charge of the lead-acid battery."

TIMCAL develops its additives in-house; Hucke says the company is looking to further improve its carbons to meet the future requirements of the lead-acid battery industry. A key area of interest is increasing the charge acceptance while controlling water consumption, and the durability of the advanced lead-acid battery.

Superior Graphite, based in Chicago, also has three purified graphite additives in its Formula BT range for the micro and mild hybrid, motive power and stationary application markets.

FormulaBT LBG8004 is a high performance, high purity graphite additive designed primarily for VRLA and flooded batteries designed to excellent cycle life and high charge acceptance under high rate partial state of charge conditions. This blend is suited to stationary applications such as



telecoms and grid-level batteries.

Superior Graphite says adding it to the negative active material will reduce sulphation and improve cycle life under high rate partial state of charge for dynamic charge acceptance applications and does not result in excessive water loss.

The second formula, 2939APH, is designed for the same markets and is a lower cost, multi-purpose additive that does not improve cycleability as much as the LBG8004. Joseph Li, product manager of Energy Materials at Superior Graphite says: "The 2939APH is a low-cost approach, and is suitable for automotive applications by combining with conductive carbons."

The third is BT ABG1010, expanded graphite for VRLA and flooded batteries to boost cycle life and high charge acceptance under high rate partial state of charge conditions. This blend is most suitable for automotive applications.

Jinkeli Corporation,

headquartered in Shandong Zibo, China, has designed a range of additives for the lead-acid battery industry. In response to an increase in lead-acid battery powered e-bikes and EVs in China, Jinkeli's engineers have developed additives to boost battery capacity, offer longer cycle life and better charge acceptance.

Jinkeli's composited additives contain high conductivity carbon, surface active lignin and humic acid. The four types of additive blends are JS Series, which is used for micro-hybrid and SLI batteries, JV Series is used for standby batteries; JEV Series is used for motive power batteries; and JSP Series which is used for storage batteries.

Jinkeli Research Centre of Battery Engineering Technology carries out its own research and development on battery additives.

"We have increased the investment in people and laboratory equipments. It will enhance the testing capability of the centre obviously, and will speed the exploitation of new additive products," says Xin Yancao, managing director of the company.

As with any new developments, manufacturers can be cautious about using additives in certain applications. Companies delivering batteries to automotive OEMs are especially wary. Klein, of Penox, explains that using new materials can mean a lengthy approval process for manufacturers of up to two years so manufacturers are stuck with the materials they are using now for the time being.



For this reason the aftersales market has been the first area to adopt additive enhanced batteries. "It was much easier to work together with companies that mainly produce for the aftermarket because there is not the same approval process that were asked by the automotive manufacturers."

Several battery producers have begun the process of having additives approved for use in automotive batteries and Penox, for one, is hoping the benefits demonstrated will shorten the approval process.

With any of the products available there is an element of compromise –improve charge acceptance but engineer the battery to overcome the deterioration in cold cranking performance. Until the ideal blend has been found, these are the options that can be beneficial to the battery maker's needs.

And what can be expected in the future? As a relatively new area of research, there will be scope for improvement. Hammond's Achim Lulsdorf says: "The requirements are constantly changing and commonly accepted specifications have yet to be determined. Our main research focus is now to develop a deep understanding of the expander component's interaction. We will certainly stay busy in this field for years to come."







Energy

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The future is electric, but is it 48V?

The Editor travels to Frankfurt's Automotive 48V Power Supply Systems conference to find out if 48V be placed alongside 42V in the file marked, 'Great idea but too expensive/complex to implement'?



hanging the voltage level of electrical systems in cars is not as easy task. In fact, it is a real pain in the backside.

The last time there was a major upshift in car voltage levels was in the 1950s, when many manufacturers switched from 6V to 12V. Despite all the positive noises at the Automotive 48V Power Supply Systems conference in Frankfurt, this author is not at all convinced the car world is about to take the huge undertaking of converting to 48V quite yet.

Automotive 48V Power Supply Systems was an immensely repetitive conference. With speakers allocated 40 minutes, this was hardly surprising.

When a conference proceedings start at 8.45 and finish at 6pm, it can seem like hard work just to stay alert. A tip for next year: less time for speakers, shorter days, please.

The message about the attractiveness of a 48V powertrain was hammered home and there is little doubt lower CO_2 emissions, improved fuel consumption coupled with more low-end grunt for faster acceleration via the benefit of electric motors in a 'mild' hybrid application are a sexy prospect.

But we've been here before, of course. 42V was the 'Great White Hope' of the automotive industry (and, of course, the lead-acid battery industry). That is now a distant memory. While 42V - three 12V lead-acid batteries in series – was never going to be the solution, the cast-iron need for 48V - mostly driven by tight reductions in CO_2 emissions - is not certain.

Car manufacturers make all the right noises but they know this is a monumental undertaking and, at least in private, they'll tell you that they'd much rather squeeze a bit more out of a 12V AGM battery if they can get away with it.

The problem is the load requirements have almost risen to the point beyond the capability of 12V. The average load of BMW's fleet has reached 250A and further increases are limited by the alternator's capacity to withstand greater load without blowing up.

BMW has a target to reduce power consumption by 50% and the German giant would perhaps rather not go to 48V if at all possible but, for its larger vehicles at least, it is seems inevitable if power consumption continues to rise. Trying to regenerate all the energy used by a 12V system in very short recharge period would require BMW to increase either the voltage or the current, which has already reached 250A. Although Sirch suggested a possibility to reach 350A, in practice this seems too high – with an alternator made from gold!

It's much 'easier' to increase voltage, said Ottmar Sirch, BMW's power network and electrification project manager. Sirch thinks there is little chance of avoiding a 48V dual voltage power supply in the next five to ten years.

However, even with this relatively lengthy timeframe, Sirch gave the distinct impression BMW was doing utmost to avoid it. Indeed, BMW has pooh-poohed the European Commission's proposal to set an average limit for new cars' emissions of 95 grams of CO_2 per kilometre by 2020 and, via Chancellor Angela Merkel, it has successfully lobbied for this limit to be delayed and watered down.



BMW 7 series





In 10-15 years, said Sirch, mild hybrids would be displaced by pure/plug-ins. Full hybrids would reach 400-800V (although this needs considerable protection for drivers, a 400V heated windscreen would make more than your hair stand on end!). BMW repeatedly hinted all this stuff was over the horizon rather than on the horizon.

What seems certain is that stopstart technology is not enough to satisfy more stringent CO₂ emission reduction targets, particularly the tougher Worldwide harmonised Light vehicles Test Procedures (WLTP). It needs recuperative energy harvesting/e-assist to get there.

BMW said 48V had the potential to reduce power losses by sixteen-fold versus 12V due to resistance. This allows power equipment components to be made with smaller diameter copper wire.

But 48V is not without problems. Aging of lithium-ion was said to be very problematic at low voltages.

Arcing looks to be a more pertinent issue. 42V cars found arcing to be a major problem; an investigation by Daimler found there is no virtually no way to eliminate parallel arcing but optimized wiring harness routing and PCB positioning can mitigate the problem.

Serial arcing can be avoided by circuit breakers. A BMW lab test

found that using a capacitor at 50A load mitigated problematic arcing. Though not totally eradicating the problem, at least prevented constant arcing.

Sirch said a 7 Series car with 48V would add between €500-1000 to the production cost, below €500 at 'serious' volume. BMW pointed to 48V offering a potential 25-30kg wiring weight reduction, not a huge amount compared to a two tonnes 7-series, but every little helps.

In general, however, BMW seems a reluctant pioneer; it is very difficult to plan the switch to 48V and OEMs need to reach all the milestones, affecting all most all parts of the car, before proceeding. BMW is also wrestling with which cars to migrate to 48V, 7-5-3 series more probable, but possibly the 1 series and Mini too.

Sirch said BMW was finalizing plans to launch a 48V vehicle, but did not specify which car it would be (though likely to be a 7 series) by 2020. However, during a coffee break chat with a representative of Thyssen-Krupp, the author ascertained that it had been working on a prototype 48V steering wheel for a 7 Series until BMW recently cancelled a tender for quotes...

Volvo

Where BMW leads the way (or not), others follow. Volvo has a target

Introduction and Motivation. Increase of electrical systems in BMW 7 series to reduce average fleet carbon emissions to 95g/km and it expects to reach average load of 250A within the next few years, up from 200A now.

Robert Eriksson, who leads Volvo's electrical propulsion architecture technical team, said while 48V will never be enough for pure EVs and plug-in hybrids, there is a now at least a 'standard' offering for 48V across the industry, i.e. 48V/12V dual architecture, which could be used in mild hybrids and possibly micro-hybrids.

While the WLTC emissions regime is more analogous to regenerative systems than the outgoing NEDC (New European Driving Cycle) regime. Yet while 48V regenerative systems deliver improved emissions, the results could not be described as dramatic.

Volvo developed a S60 prototype with a 48V lithium battery, 48V electric motor, 48/12V DC-DC converter and 48V electric distribution with a standard S60 diesel engine, bringing up weight by 5kg.

The result was a reduction in CO2 emissions from 140g/km to 131g/km on the NEDC cycle and from 155g/km to 143g/km on the WLTC cycle, while increasing acceleration by 2.7 m/sec to 4.2 m/sec over 0.3 seconds.

Volvo has been grappling with various options for mild hybrids– should the regenerative system be connected to the wheel or belt connected to the ICE? Wheel connections are much more efficient in recovering energy during braking, but ICE-connected systems can be harnessed at speeds of up to 100 kph.

The Swedish car maker is also struggling to find a way to integrate a 48V system with existing 12V components. In an ideal world, there would be two sets of components, one 12V, one 48V, but of course this would prohibitively

expensive and heavy.

So a 48V must be treated as a completely new system rather than a 12V system with four times the voltage. Like BMW, Volvo has found arcing to be a problem, but in the lab it found capacitors in the DC-DC converter practically negated the issue of serial arcing.

Eriksson finished his presentation by noting that while the automotive industry is on the limit of 12V, it is not at the end of the line...

Bosch

Like the car OEMs, Bosch sees the big push for 48V coming from CO_2 reductions, not least the switch from NEDC to WLTC, and from 2018 it sees a real momentum gathering behind it. WLTC allows fewer cycles but more decelerating and longer periods of braking – that is why CO2 figures register higher than under NEDC.

Bosch is developing a 'Boost Recuperation System' (BRS), a 10 kW @ 48V unit that offers an 8-18g/km CO2 reduction. BRS works by 'downspeeding': working with the engine to reduce RPM without additional gears.

Bosch doesn't believe there will be a total switch to 48V.

All OEMs are discussing 48V, not

all will use it but all are considering it, and not just for premium vehicles, but also for mass market cars too.

There were more than a few eyebrows raised, however, when Boris Kuhlmann, of Bosch's starter motors and generators division, projected 1.25m 48V cars on the road by 2018, and 3.25m by 2020.

Ricardo

British engineering firm Ricardo also sees mass market mild hybrids, including 48V, as inevitable over the next 10-12 years due to emerging hotel and ancillary loads.

For a firm like Ricardo associated with gas-guzzling motor sport, the sexy bit of 48V is the opportunity to give cars more low-end grunt, with faster acceleration and fuel cut-off at lower speeds, also opening up the possibility of downsizing engines thus further lowering emissions.

The industry rule of thumb is that it costs OEMs €50 per gramme CO2 saved, 48V could add €2000 to customer OTR price, meaning it may be something of a premium product.

Ian Whiting of Ricardo's hybrid and electric systems division said all the necessary components such as batteries, inverters, DC-DC converters are there, but credible system costs remain a challenge. Whiting, rightfully, questioned if the 10-15% reduction in CO_2 allowed by 48V was really enough in the long term?

Of course, 48V does not necessarily mean lithium. Ricardo is involved with the HyBoost 2 project, involving Ford, Valeo and ALABC, utilizing an advanced lead-acid battery in a Ford Focus. However, this rather uninspiring project involving not a lead-acid battery firm but a lead-acid trade association may be little more than a 'Don't forget about us!' ad for lead.

Whiting noted that a 12V leadacid battery plus supercap allows 10% regenerative power, but with torque assist and a 48V battery, OEMs can further downsize engines.

Ricardo has developed its own lithium packs using A123 cells, which it says offer 120 000 miles of 8 years life under 'normal' driving conditions. Although frustrated with having to keep lithium within the 60-80% depth of discharge envelope, Whiting doesn't really care what the battery as long as it can do the job and does not add too much weight...

Continental

Continental is renowned as a tyre manufacturer, but that is by no means all it does. The German automotive supplier has developed a 48V lithium-ion automotive battery pack in a joint venture with Korea's SK Innovation, called SK Continental E-motion, which began operations in January 2013.

For this venture, SK Continental eschewed industry standard lithium iron phosphate for NMC, due to the former's hard-to-handle anode, flat voltage and relatively unimpressive power density. LMO is too prone to aging due to graphite electrode damage, while despite high power density, LTO was deemed too difficult to perform to a consistent standard.

The German-Korean joint venture also plumped for pouch cells due to improved safety, costs



Market trends in

different vehicle

classes

and cooling, although this is offset somewhat by a shorter lifetime versus hardcase cells.

SK Continental has found it a challenge to fight the right current collectors for its 13-cell (6Ah/10Ah) 280Wh/460Wh NHC packs, while conductive material is also problematic as it is "attacked" at high voltage. Whether this pack is targeted for use in 48V cars was not certain, they may find a more suitable home in industrial electric vehicles.

Automotive 48V Power Supply Systems' panel discussion focused on the technical and practical problems of implementing 48V. There is an almost infinite range of topologies for a car's 48V system architecture, we heard.

GM has its own 48V spec, while Toyota use three voltage levels for some of its 288V Lexus models. It is clear that there is no one-size-fits-all solution and it will be a case of 'horses for courses'.

At one stage a debate broke out about which components should be 12V and which should be 48V. BMW wants 48V components to be able to withstand a maximum voltage of 70V due to cycling spikes, particularly on start-up.

There was also debate about how the powertrain should be comprised. Different Tier 1 suppliers have different ideas about how the powertrain should be devised. Bosch does not believe in a starter motor for small cars, believing its BSG (belt-driven starter generator) is sufficient; Audi, for example, does, due to a lack of torque and possible cold start problems.

In 2011, Germany's 'Big Five' – Volkswagen AG, BMW AG, Daimler AG, Adam Opel AG and Ford-Werke GmbH announced a programme to develop a dual architecture 48V system. A draft 'LV148' spec has been distributed to OEMs and suppliers, and LV148 is due to be updated following analysis of the resultant feedback, but as yet there remains no harmonized 48V spec.

The lack of standards is a problem for a move to 48V. Equipment manufacturers think 48V is a great idea, as they could sell a load of new kit, but car manufacturers are not nearly so sure.

Christian Kunstmann of Adam Opel AG even wondered out loud whether 48V is the best voltage level, and although the industry had the required 48V technology, do car manufacturers really want to use it? There were also questions as to the unproven lifetime expectation for 48V systems.

In contrast, Frost & Sullivan's power supply systems expert Prana Tharthiharan was highly optimistic about 48V, perhaps Examples of enhanced power requirements of board net and electrification of devices



seeking an opportunity to flog more of the market intelligence firm's (questionably useful) 'crystal ball' reports. Tharthiharan's crystal ball looked a little cracked in Frankfurt, as his presentation looked dated in light of revelations about OEM's slowing progress.

Tharthiharan sees a 48V tipping point at 3 kW load and cited 2020 as the magic year (as so many others do in so many energy-related industries!) when it will become standard, with 2m European 48V vehicles expected on the road.

As for battery technology, well, Tharthiharan forsees big things for AGM lead-acid batteries, but he dropped a clanger by citing the Volkswagen-Valeo-ALABC 'LC Super Hybrid' project as lithium's superiority for 48V. As ALABC's Allan Cooper rightfully pointed out, the 'LC' in 'LC Super Hybrid' stands for Lead Carbon!

It was not all positive. Tharthiharan lamented the lack of suitable suppliers and he highlighted the move to 48V is largely a European phenomenon, with US OEMs showing almost no interest at all. However, it was also noted that Chinese OEMs and suppliers are actively developing a single voltage architecture for 48V...

PSA

Amid great fanfare, France's PSA (Peugeot-Citroen) announced in January 2013 it would launch an 'Eco-Hybrid' car in 2017, combining a 10 kW electric motor with a 48V lithium battery. At Automotive 48V Power Supply Systems, however, the poor bloke in charge of simulating electromagnetic compatibility (EMC) at PSA was less than enthused with 48V.

Salah Benhassine went into some detail into just what a pain in the arse a switch in voltage would be in terms of designing a car to accommodate 48V in terms of EMC. Make no mistake, delegates



undertaking for the electrical systems, requiring new PCBs, cable shielding, wiring harnesses and so on.

The DC-DC converter and 48V batteries need a shielded enclosure, and it is difficult to incorporate this

the 48V system components for EMC challenges

problems. While not insurmountable, the need for filtering to mitigate magnetic induction is difficult to achieve, requiring dedicated R&D programmes and partnerships, as traditional cable shielding is not effective.

EMC problems and the need for more research are just one reason why the progress of 48V will be slower than the likes of Frost & Sullivan suggest. Driven mainly by EU emissions regulations, which are a moveable feast, means 48V looks on relatively shaky foundations.

Without cable shielding, current

places which may cause passengers

is distributed to doors and other

As one delegate told me, "Now is the right time to start to think about 48V". I believe he was right. 🗘



machine

shielding from both sides in the

highly problematic.

'global box' [see diagram] and this is

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Batteries an afterthought at EVS27



Ruth Williams is disappointed by the lack of battery content at the 27th edition of The International Electric Vehicle Symposium & Exhibition (EVS) in Barcelona. Just like EVs in many respects, the show was found wanting in the basics.

eople visit Barcelona for the weather, food and to see the architectural touches of Antoni Gaudi that adorn the city. What visitors may not realise is the push the Spanish city has made to reduce CO₂ and increase the number of electrified vehicles on its streets.

The week of EVS27 brought torrential rain that made seeing Gaudi's buildings difficult; so there was nothing to think about but the EVs.

The city boasts more than 300 EVs in public fleets, including street-sweeping trucks that move silently through the narrow streets. The packs of bumbling tourists take a long time to notice their looming presence, which seems a fitting analogy for electrified vehiclesthey are slowly creeping up on us and most people do not notice.

The venue had space for the 232 exhibitors and 4 000 visitors in attendance, and the centre of the hall was taken up by automakers showing off the latest electric or hybrid models. Bringing a sexy car

and pretty girls to talk

about the car seemed the best way to attract attention of visitors and increase footfall to a stand. The side avenues of the hall were comparatively hushed as people gravitated towards the shiny vehicles.

Being an electric car show, these will tend to pull the crowds. The ancillary supply companies can hope to attract the wayfarers, but it is tough competition. And while everybody seems pleased with the attendance, it begs the question if this is the right place for battery makers? Or are they getting lost in the crowd?

A big positive for the exhibitors was the long lunch break each day, which gave plenty of time for delegates to visit the stands and test drive the collection of EVs in the car-park.

The first session of the conference featured Olivier Onidi, the European Commission's Director of Innovative & Sustainable Mobility, who welcomed the audience with this opening gambit.

NAUD

"We have come here to learn what is bringing the best results from all the

ideas and designs that are out there at the moment." Quite a promise to live up to.

In lieu of a hardcopy programme, there was an EVS27 app to download on arrival. Unfortunately it had limited information beyond session times and who was speaking. Not even all the presentation titles appeared to be included, let alone a summary.

This left delegates planning which sessions to attend based on luck. Another annoyance was the sessions took place in partitioned rooms of the main exhibition hall that did not eliminate much background noise and, worse, often resulted in two sessions being audible at once.

In the dedicated battery track the majority of the presenters were students discussing their work, while the names and companies on the programme who sounded interesting were session chairpeople rather than speakers. Why two co-chairs were required to fill this role was a mystery.

The highlights from the battery sessions included Dan Radomski, director of market development of NextEnergy, speaking about

JUALCOMM

Oualcomm was

exhibiting the

Spark-Renault SRT_01E single-

race car, which

will be used in

the inaugural

Formula E race

series

seater, all-electric

how the supply chain dynamics within the US could be improved for domestic lithium-ion production. Radomski says there is a global overcapacity for automotive lithium-ion batteries, this has ranged between 300 – 1000% but vehicle production to actually use these batteries is picking up.

Asia is handling all the demand for components at present; Radomski says any 'would-be' US suppliers are restricted by lowvolume production, so they lose out to Asian competition. The window of opportunity lies with short shelf-life products such as salts, additives and solvents for the electrolyte and copper foil for current collectors. Shipping time from China is too lengthy for these components to be useful when they arrive on US shores, so domestic supply would assist cell and pack makers.

Interestingly, there was no talk of range anxiety for EV drivers; this problem seemingly is now at the feet of charging companies and networks rather than battery makers. One of the major themes of the battery track was that battery performance is hampered with the ageing of cells. With the cost of an EV being largely due to the high cost of the battery, if said battery is only good for eight years then the vehicle is a less than prudent investment.

There was a host of presentations of graduate and post-graduate work testing cells and batteries at different states of charge. The trouble was the work is preliminary and often just the starting point of something more comprehensive.

For instance, Rughavendra Arunachala of Brussels University discussed the start of his work on cycle life characterisation of large format lithium-ion batteries. Arunachala identified these as the

best option for EVs because they offer high energy and power but have less wiring to go wrong!

He discussed his findings of putting lithium (nickel manganese cobalt) oxygen cells inside a climate chamber, showing cell temperature increased as the cells aged. He concluded by saying the reasons for the ageing are not known and more detailed studies will be required.

Similarly Genki Kaneko, a student at the Waseda University in Japan, presented his work addressing degradation mechanisms of lithium iron phosphate batteries. He pointed out that while LiFePO4 is good for charging and cycling, it suffers from degradation of cells over time. He found by testing batteries at higher temperature and state of charge (SoC) increased capacity loss and caused more degradation. Kaneko said temperature had a greater effect than SoC and that capacity loss is due

to chemical reactions. Using batteries at lower temperatures and SoC will extend the battery's life but it won't perform as well.

Top to bottom:

The **Porsche Panamera S E-Hybrid** plug-in hybrid EV with a 9.4 kWh lithium-ion battery combined with a 3-litre supercharged engine. It emits just 71g/km of CO_2 — unheard of for a car of its class

The **Volkswagen XL1** plug-in hybrid that comes with a 5.5 kWh capacity lithium-ion battery combined with a 2-cylinder combustion engine. VW quotes up to 31 miles of all-electric driving range

The **BMW** is is the first all-electric offering from BMW has a range of between 80 - 100 miles and emits just 13g/km of CO_2

The **Renault Zoe** has a 22kWh lithium-ion battery that delivers a range of 130 miles. It is the top selling EV in France with sales over 5 000 units from December 2012 to November 2013

The **EDI Auto T300** is a Chinese-made threewheeler that can hit 125mph with a price tag of \$50K. But it does look like the Batmobile and attracted a lot of attention to the stand

The optimised charging to extend battery life would be at 24% for warmer climates and 38% SoC in colder weather. The drawback is this has been based on calculated data real world testing is required for validation.

These presentations showed that electrochemistry students performing extensive testing on cells and modules are making incremental gains in battery performance, but there were no big breakthroughs or developments from companies to shout about.

The various presentations sought to establish the optimum working conditions and ideal configurations to get the most out of cells, modules and packs in an EV. The limits of each study leave scope for continued research for many years to come. If nothing else, it shows the impressive numbers of on-going battery studies and just how many eager students are waiting to begin a career in electrochemistry.

Boys toys: This

e-scooter from

Dutch Virto was a

great break from

iron phosphate

the conference hall.

It features a lithium

48V / 10Ah battery

that riders can

whizz about on

at 25km/h

on public

roads-

in the

great fun

Spanish

sunshine

three-wheel

To be fair to the research students, they presented their work well, but it seemed out of place at the world's biggest international EV event. It probably

did great deal for the students' own work prospects and hopefully some cell and pack makers were listening with perked ears to facilitate taking the work to the next level.

So what else was there? Well, Norway is the 'poster girl' for EV success: It has the highest number of government-backed buying incentives of any country in the world. They include exemption from taxes, use of bus lanes, free ferries and free parking, which have been in place since 2003.

From 2014 new incentives will include VAT exemption for EVs and batteries. This push has worked – there are 3500 EVs in Oslo and 16 000 across Norway; in September 2013 8.6% of cars sold in Norway were EVs, 7.2% in October. The Nissan Leaf was the country's best selling car for October 2013.

The other big issue was charging, so it was fitting that Qualcomm was a global partner of the event and held the most prominent position in the exhibition hall. No one could fail to see the racing car from the newly unveiled Formula E series, in fact, this was the first time the actual car rather than a model had been exhibited. It was positioned over a Qualcomm charger, as partner to the E-race series that starts in

September 2014.

Qualcomm's VP of business development and marketing Anthony Thomson spoke about the company's wireless charging that uses resonant magnetic induction system to automatically charge a car parked over the sensor. It would remove the barrier to the uptake of electric cars, which is in Qualcomm's view, is the lack of charging infrastructure.

Working with Formula E Holdings on the race series, the company will develop its charging system for use with road and passenger vehicles. Thomson argued that charging little and often was a better way to get cars on the road and fitting in with customers' driving habits instead of an overnight mega charge.

Senan McGrath, a member of the Task Force EV division of European electricity industry association Eurelectric, addressed the issue of whether the electrical grid could even cope with charging requirements of mass uptake of

EVs. By Eurelectric's calculations, if there were 100% EV uptake, the KWh capacity for the

40

continent would need to be increased by 20%, individual countries would only need a 1% increase in electricity supply – achievable in anyone's eyes.

McGrath said if charging of cars could be guaranteed to take place off-peak then no change would be needed. He added 10% of all cars would have to be an EV before the grid notices any impact.

The argument EVs merely move the emissions from the tailpipe to the power station was counterbalanced by McGrath with calculations that even if the electricity came from coalfired power stations it would still achieve the 2015 Europe-wide goal of lowering carbon emissions to 130g/km. Using gas-fired power stations could reduce CO2 to 56g/ Km, using wind power to make electricity could reduce it further to just 9g/km.

McGrath concluded Eurelectric sees the significant savings that are possible with the widespread adoption of

electric cars but stressed that utilities must be heavily involved in any discussions on EVs and charging.

The classic 'chicken and egg' argument about electric cars and charging stations gave some interesting insights. Takashi Shirakawa of the Nissan Technical Centre Europe said their customers' habits show they charge at home rather than on the road, so infrastructure is less important.

It seems a short-sighted view that this behaviour would remain if all cars were electric, especially in cities where residents are far less likely to have a driveway or garage. Qualcomm's Thomson had a more rounded view that yes, people will charge at home but if this is their prime car they need to be able to charge it wherever and whenever they need. He says: "You wouldn't buy a petrol car if there were no petrol stations." Too true.

In the spirit of being an international conference, it is fitting to address the need for a universal charging system that is

suitable for use anywhere. A consortium from SAE, the international society of automotive engineers, has

> Looking inside the Nissan Leaf: Over 62 000 of these have been sold globally since 2010 and US order have doubled for 2014 based on sales from last year.

developed just that.

Their Combined Charging System combines common AC charging with DC fast charging in one system. Robert Weber of BMW talked about the single system that means EV drivers only need one charger regardless of where they are in any country or continent.

Weber said the system is safe and robust: if anything goes wrong it will shut down. The amount of current drawn is controlled at the connection point that has both AC and DC charging options for long overnight charges or opportunistic fast charging.

The development is supported by all the major automakers in US, Europe and Asia and is not subject to license to encourage universal use. International standards associations including SAE, IEC and ISO have been involved throughout the design process so the charger can be used and sold globally.

Cornel Pampu, manager of the combined charging office at Carmeq GmbH, reinforced the importance of a universal charging system; he says making the system user-friendly and compatible with driving-styles is as important as the connections themselves: People need choice and flexibility – they get that from petrol cars so to replace petrol cars the alternative must be as at least as adequate and flexible. *Will fast charging become a key selling point?*

It seems EV fans have been overly optimistic about uptake numbers. Changing the driving habits of billions is ambitious. However, as technology and aesthetics improve the cars are starting to sell, as Norway has demonstrated, we are slowly seeing them creep into everyday life.

From a battery-centric viewpoint, as a core element to any discussion on electric vehicles batteries getting more attention at EVS would be just. •







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IRES 2013:

Disneyland in Berlin? No? Well, we'll let you in on a secret. Once a year, the Berlin Congress Centre is transformed into a magical fantasyland where solar power is the answer to everything, fossil fuels and nuclear do not exist and where money grows on trees.

The Berlin Congress Centre (BCC) is no stranger to propaganda. Sited under the shadow of Berlin's TV Tower adjacent to the former Interhotel Stadt Berlin in Alexanderplatz built for Comecon representatives – now owned by Radisson – the BCC is in the heart of what used to be the German Democratic Republic's East Berlin.

In the understated elegance of the plenary hall, the 500 International Renewable Energy Storage (IRES) 2013 conference delegates were subject to an orgy of speeches, promising a future German energy system powered exclusively by renewables. Renewable energy is the answer to

bestshowreport 67Do they believe in

The Editor visited Berlin for the 8th International Renewable Energy Storage event and finds a decent conference spoiled by far too much solar power propaganda.

everything, it seems: renewable energy to heat, renewable energy to gas, renewable energy to liquids, renewable energy to propulsion.

fairies?

In other countries this type of speech would be made by the kind of lentil-loving deep green environmentalist who refuses to wear sandals if they are made of leather. In Germany, they are made by politicians.

Of course, it is very easy for a politician to promise 100% renewables by 2050, particularly when it is 36 years away and they'll probably be dead by that time, let alone still be in office.

But Berlin in late 2013 was an uncertain time for the renewables industry. The coalition was still deep in negotiation to hammer out their policies and the industry was not expecting changes to Germany's iconic ErneuerbareEnergien-Gesetz (EEG, Renewable Energy Act) until well into 2014. Indeed, Federal Environment Minister Peter Altmaier – effectively the minister for the *Energiewende* or energy transition – was negotiating a new coalition



government instead of addressing IRES 2013, as anticipated.

Delegates spoke in angered tones of a possible solar power tax and there was even speculation that the EEG could be scrapped altogether under pressure by the SPD, which passed it into law in 2000, to support Germany's large coal industry and its trade unions.

So the opening and plenary speakers wasted no opportunity to hammer home the message: "believe only in solar and wind power and absolve yourself of all mortal sin".

IRES was founded in 2005 by German trade association Eurosolar, whose mission statement is to replace fossil fuels and nuclear power with renewables and this must be remembered when attending IRES. Yet the author has never heard so much idealism in a conference chamber.

Peter Droege, President of Eurosolar, opened the show with a speech invoking the TV Tower as a totemic symbol of the communications revolution of the 1960s commemorating Berlin's "openness to new ideas".

Whether this was tongue-incheek or not, the opening speech was far from open, as it was stridently anti-fossil fuels in setting out Eurosolar's perceived necessity for energy storage – Droege even used a photo of Venus. The message was clear – no storage, no atmosphere, no humans!

For some at IRES 2013, energy storage is about saving the planet. For others, it's about making best use of scarce resources, or at least avoiding waste.

Germans hate waste and is one reason why she is pursuing 'windgas' - turning wind power into hydrogen via electrolysers to feed into the national gas grid – however inefficient or expensive or impractical. IRES2013 delegates (above) were bombarded by propaganda at the Berlin Congress Centre (below) in the heart of what was the Soviet sector of the German capital The 'power to gas' element of energy storage featured heavily at IRES 2013, but batteries are what BEST is primarily interested in and there was a decent conference stream dedicated to batteries and battery storage.

However, it was not an audience of battery experts, and speakers sensed an opportunity to champion their particular chemistry to young battery 'virgins'. And as such there seemed to be a game of who could get away with telling the most naughty fibs.

FIAMM tried to claim its sodium nickel chloride were not government supported until questioned about it (although it is touting its SoNick products to mining companies with some positive feedback).

The ubiquitous Boris Monahov of the International Lead Zinc Research Organisation/ALABC almost failed to mention that the dramatically improved performance of the lead-acid UltraBattery is down to the hybrid supercap component.

Meanwhile, BASF pushed a product that does even exist: 'advanced' nickel metal hydride batteries with 7 000 cycles at 80% depth of discharge versus 3 000 cycles for 'commercial' NiMH. Yet, as Michael Zelinsky was forced



to admit to the audience when questioned by the author, his promised "new positive plate materials" are years away from commercial reality.

Oddly, there was no lithium-ion presentation even though most independent analysts view it as probably the best bet for energy storage. Yet there was no shortage of presentations about flow batteries, in theory a good fit for grid-connected storage.

US developer EnerVault seems to be making headway with its 'Engineered Cascade' stacks – in series rather than in parallel – to allow what it calls 'steady state' electrolyte continually circulated through the stacks, obviating expensive ion exchange membranes for cheaper ones.

By minimizing 'side' and 'shunt' reactions, EnerVault claims a tenfold reduction in parasitic reactions rate, meaning ironchromium is a commercially viable product. EnerVault has scaled up a 2.5 kW system to 27 kW production, tested for eight months with no leaks – so far!

Next up is the 1 MW ARRA project funded by the US DoE. This is a 250 kW, four-hour system utilizing nine engineered cascades. EnerVault founder Craig Horne is hopeful of a getting a piece of the Long Island Power Authority's tender for energy storage, but with a requirement of 12 hours storage the footprint may be too large to be attractive.

Flow batteries were seemingly flavour of the month in Berlin, and IRES was promoting the International Flow Battery Forum which takes place in Hamburg on 1-2 July.

However, not all presentations were positive.

Ireland's Dundalk Institute of Technology experience with a 500 kWh zinc bromine flow battery connected to its wind turbines was Marion Perrin reads the runes for flow batteries



highly unsatisfactory.

The zinc plate on the anode is seen as a disadvantage for wind power applications and Ray Byrne of Dundalk's Centre for Renewable Energy said the residual solid zinc buildup on the plate requires a deep discharge. Unfortunately this can mean a reduction in the round trip efficiency to a point where the battery offers a net cost rather than a benefit.

The stacks are undoubtedly a weak link in flow batteries. They are subject to dynamic fatigue, exposing the surrounding area to highly corrosive electrolyte leaks. Needless to say, Dundalk Institute of Technology is not keen on acquiring another zinc bromine flow battery for the foreseeable future.

The Institute may not be seeking a hydrogen-bromine flow battery either if Israeli firm's EnStorage mildly alarming presentation is anything to go by. Unveiling a missile-shaped system – hydrogen in a tank pressurized to 150 bar sitting on top of the electrolyte – EnStorage's prototype looked as if it could be tilted 45 degrees and be deployed in the Sinai desert against Iran in an emergency.

The EnStorage flow battery utilises only one electrolyte pump and tank. The electrolyte flows in the same direction, whether charging or discharging and features a proprietary membrane with 'in-house production'.

Rushing in where angels fear to tread, EnStorage's Itai Karelic revealed a 150 kW system would eventually cost \$330 000, having worked their way down from \$1.5m first-of-a-kind cost and \$550 000 with 10 MW/year production. Hmmmm....

Far more impressive was Vanadis Power's flow battery with a newly-developed 'advanced' electrolyte: essentially hydrochloric acid (HCL). Founded in late 2012, Vanadis Power promises energy density of 30W/litre - twice that of 'conventional' electrolyte with an operating temperature of -10°C-60°C as opposed to the current +10°C-35°C range.

Vanadis, which licenses the 'supercomputer-designed' electrolyte from the Pacific Northwest National Laboratory and use stacks made by Germany's Rongke Power, expects to deploy

its first, improved system at a substation in the second half of 2014.

With a battery response time of o.8 milliseconds, a footprint onethird of conventional flow batteries and a 20 year design life, Vanadis Power is targeting a piece of the lithium-ion energy storage systems.

Its only concern is the price. At €750/kW, Vanadis feels the price is still too high for utility customers, but if it can reduce the cost to its target of approximately €400/kW, it feels it is onto a winner.

But one must wonder if Vanadis Power may run into public acceptance problems once it realises flow batteries are essentially tanks of tens of thousands of gallons of stuff their chemistry teachers warned about. And with HCL being extremely corrosive stuff, won't do much for the stacks...

Domestic battery energy storage was another key theme of IRES 2013. In truth, this was a little bit of a beginners' guide to home energy storage and again ripe for pulling the wool over impressionable young renewable energy professionals.

Many distribution grids are at the limit of the volume of solar PV it can handle, battery energy storage could enhance the grid without building new power lines, transformers and so on. Perhaps surprisingly, the message from SMA Solar, which is involved the putting together of hybrid power plants in remote locations, was an advocate of lead-acid for domestic energy storage.

Aleksandra Bukvic-Schaefer of SMA Solar, said it would be foolish to write off lead-acid despite its status among renewables types as a deeply unfashionable 'old' technology. Being a tried, tested and cheap battery chemistry helps lead-acid's cause a great deal, as does suitable cells being sized in a wide range of 50Ah-3000Ah – handy for suitably sizing energy storage projects.

Bukvic-Schaefer said 1500Ah lead-acid cells in a 48V configuration up to 20 kWh was the best option. Just don't expect a lead-acid battery system to last 20 years, particularly without



intelligent energy management system!

In general, there were too many academic presentations and some were not well received. Michael Schreiber of Fraunhofer IWES's 'Capacity-dependent tariffs for a grid-benefitting storage operation in private households' presentation, which proposed moving away from solar feed-in tariffs went down as well as if a vegetarian had broken wind in an elevator.

The author heard the words 'perfect' too often. Many presentations featured mathematical formulae that 'proved' a particular energy storage technology is technically, if not economically, feasible.

Bosch had a go with a talk which unsurprisingly concluded that to increase the yield of solar energy, a larger battery system is preferable to a small one to increase the volume of stored energy and slow the effects of calendaric aging. So, just in case you are not *alles klar*: that's larger battery, longer life, more cash in the bank for Bosch!

With conservative estimates of 48 GW solar power capacity installed in Germany by 2020 – some forecasts see 60-70 GW – you may think the great and good of the energy storage would be desirable... Unfortunately unless the batteries can be charged at peak time of solar generation, electrochemical energy storage is not especially helpful, according to Alexander Zeh of Technical University Munich.

Zeh is seemingly one of a number of research institutes looking at curbing the feed-in rates of solar. This one focused on exploring home battery storage systems configurated to assist grid companies, i.e. the batteries are charged at peak generation to keep grid load within maximum limits.

This would require batteries to be discharged at night to prevent a full battery in the morning. But

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isn't this the whole of point home energy storage?

Zeh calaculates the financial benefit of a 5 KWh battery energy storage system connected to a 8.7 kWp solar PV system is only €200-300 per year assuming a power price of €0.34/kWh and feed-in tariff of €0.12/kWh. With a lithium-ion system costing at least €1000/kWh, at this kind of price level energy storage could be seen as only a vanity project for the rich or foolish.

A123 Systems served up some interesting fare with their trial grid reinforcement projects as part of the UK Low Carbon Networks Fund, installing lithium storage in both 40-feet containers and UPS-style racks in various cramped and decaying substations in Northern England.

Speaker Roger Lin said the market for lithium-ion energy storage is highly limited for fully commercial projects, but regulated utilities – particularly in the United States - have expressed a growing interest in acquiring portable, containerized energy storage units to be transported around their networks to alleviate congestion as and when required. Lin also hinted that A123 would unveil a large format cell with significantly improved power and energy density in 2014, possibly with silicon.

In some sessions, the average age of the delegates was barely higher than a typical University lecture theatre. The poster award winners all looked under 30 and were pure academia, with titles like 'Optimal Deployment of Power to Gas in the Context of 85% Renewable Energy Scenario."

Frankly this was stuff that would make even the most strident vegan sandal-wearing green blush. But, at least, you have to credit Germany for having a national plan – the *Energiewende* – and inspiring young people to join in and try and change the world.

Here was a conference free of the usual 'evil capitalist' buzzwords of 'capex', 'opex', 'ROI', 'profit' and 'loss'. Many speakers simply did not care if their particular project would require everyone to forego the wearing of shoes to be able to afford it. As long as it is technically feasible, that was OK.

Tobias Rothacher of Germany Trade & Invest was one who had


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undoubtedly drank the Kool-Aid. Speaking of a tipping point sometime between 2016-18, when the return on investment from solar panels alone is exceeded by solar plus storage, Rothacher rather brazenly predicted "most PV systems will be installed with a battery when the FiT ends".

This was possibly the most 'sunny' presentation in an extraordinarily optimistic/deluded conference. The infantile debate was encapsulated by a press conference to discuss a press release stating that hydrogen had the potential to offer enough energy storage for three weeks of German demand.

When the author queried why an organization dedicated to solar power was suddenly extolling the hydrogen economy he was informed that the press release was erroneous and should not have been published.

When pushed further on the matter, it emerged the press release was the subject of an internal IRES steering committee debate and it informed the conference organizer to suppress it and delete the article from their website. This was all getting far too Orwellian, but this was nothing compared to the panel debate on the middle day.

The discussion was titled, 'Where and how will energy storage be taken into account in future energy markets?', but here once again there was far too much political posturing by academics and lobbyists about solar rather

The tiresome

panel debate was

yet another solar power propaganda

exercise rather than

an energy storage

discussion

than discussion about storage.

Claudia Kemfert, Head of Energy at the German Institute for Economic Research, said that over the next four years the German federal government would only be interested with short-term priorities and the only priority is the *Energiewende* and increasing deployment of renewables. Therefore, she said, there is no hope that the new Government will make a push for energy storage.

Others were was even more blunt, saying politics solves genuine problems, and storage is not a problem – Germany doesn't need it, so we shouldn't ask the Government to support it. The implication was clear – there will no slice of the cake for storage, and we couldn't really care less.

But the solar lobby cannot have its cake and eat it. If there is no need for storage, why is the Government discussing a capacity market to ensure enough dispatchable generation to keep Germany's highly industrial economy powered?

An 'energy-only' electricity market based on zero marginal cost generation cannot and will not reward investment and continued operation of dispatchable generation to power the world's third-largest economy. Either there is enough electricity capacity or there is a need for storage and/ or capacity market, but both of these statements cannot be true simultaneously.

Dirk Uwe Sauer of RWTH Aachen

University injected some reality. Recognizing that an energy-only market would ensure zero marginal cost generation would always out-compete storage, Sauer saw the need for a capacity market to reward power which is available but not generating power.

However, a capacity market is doubled-edged as it opens to the door to new investment in fossil fuel generation, gas and coal, which would also likely out-compete storage unless the market is designed accordingly.

Sauer estimated that with 100% wind and solar, Germany would require between 30-50 GW of storage for 2 hours per day, equivalent to 50 000-100 000 20-feet containers of 1 MWh lithium-ion batteries.

However, it should be noted that storage is not currently economic as a hedge against peak power prices; the differential between the high/low in Germany is currently just €0.03/kWh. Interconnectors and cross-border trading are also seen as a major obstacle for the widespread deployment of energy storage.

In general, there does not seem to be much of a lobbying effort for energy storage in Germany. Indeed, the president of the German Energy Storage Association, Eicke Weber, barely mentioned storage during the opening keynote speeches, instead using his time to extol the virtues of– what else?– solar power.

On the final day of the conference Evonik discussed its



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lithium-ion energy storage project in the southwest German town of Volklingen-Fenne, where it has connected a 1 MWh system at a 10kV substation in the mediumvoltage grid.

The Lithium NMC cells are made by Litec, its subsidiary joint venture with Daimler, using proprietary Separion ceramic separators for lithium-ion applications. As opposed to, for example Duramic's plastic lithium-ion separator Celgard, which are resistant to around 134 degrees Celsius, Separion can withstand up to 220 degress, although it remains to be seen whether the extra costs and weight will prove attractive.

From a 12-month dataset, Evonik calculates its 500 kW/1MWh system could muster the 7 000 cycles necessary to provide primary control power in Germany. With project developers like Younicos using Samsung SDI lithium-ion guaranteed for 7 000 cycles over 20 years, however, Evonik may have undersized its system a touch.

TECH TOUR

Despite IRES 2013's shortcomings in terms of content, BEST could not fault the organization of the event and the opportunity to attend a technical tour is always welcome. As with the conference, however, the excursion to see a battery energy storage system by system integrator Durion – essentially a poor man's Younicos - was disappointing.

The tour was to the site of a closed district heating plant in the

German energy storage integrator Durion learned the hard way that Chinese lithium-ion quality control lags behind its East Asian neighbours



Peter Droege, President of Eurosolar opens the anti-fossil fuel proceedings Alt-Treptow district of what was East Berlin. The system is connected to the 10 kV medium voltage network and this probably explains why the plant has been closed, as the medium-voltage network in the 'Allied' zones are 20 kV networks.

The 2 x 1 MWh lithium iron phosphate battery modules are housed in containers with integrated transformers. The system features a Siemens' Sinamics power management system, with a Fraunhofer-designed BMS system.

Unfortunately, the system was not operational due to battery module failure, meaning it had not passed the pre-qualifiacation process necessary in Germany at the time of the visit. The Sinopoly lithium iron phosphate cells had unstable power output and were replaced under warranty.

As a result, Durion says it will use Lishon lithium-ion batteries for its next energy storage project. This was an expensive reminder that Chinese quality control still lags behind the fully-automated manufacture of Korean and Japanese cells and representatives of Younicos present on a spying mission would have little to be worried about.

Younicos has exclusive arrangement with Samsung SDI for lithium-ion battery energy storage projects in Germany, which may be more expensive than Chinese lithium battery packs but do generally function correctly.

When operational, Durion expects a 8-10 economic life, though technical life is theoretically 15 years due to low system stress; the batteries usually run in a +/- 5% state of charge envelope.

So, in summary, there is no need for Disneyland in Berlin.

Merely pop along to the BCC for a renewable energy conference. Who knows? You may even come to believe in fairies. •

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Saueressig puts the pressure on lithium-ion electrode performance

Gerry Woolf pays a visit to Saueressig in Germany— a new European player in the world of advanced battery toolmaking.

The world admires the results of German engineering but what underpins its success? Three things: excellent training, excellent education— and great toolmaking. At BEST magazine we have looked closely at the German industrial effort to make electric mobility happen. We have alluded to the fact that there is not much of an indigenous advanced battery industry in Germany yet.

But at February's Battery Japan show in Tokyo, still the vanguard event for manufacturers looking to select lithium ion manufacturing lines, there will be a clutch of companies on the German pavilion.

One of them will be Saueressig, part of multinational Matthews Brand Solutions.

This is the company that is the leading player in very large format

printing on products you do not think of as printed— like floor and wall coverings. But then everything you buy has packaging, printed on paper, card and plastics.

Saueressig are specialists in printing technology for these more unusual materials and it is only when you see the machines used for this work that the connection between calendering lithium-ion electrodes is obvious. Both need heavy roller based processes to achieve the desired effect applying high pressure to material surfaces with great precision right across their width.

Many companies look for new markets to take their existing technology but Saueressig's move into building machines for the advanced battery industry was brought about by a search by one of its customers - the now sadly bankrupt Finland-based European Batteries - for suitable Europeanmade equipment. Saueressig has since built a similar machine for Germany's Varta Batteries.

Rising to the challenge, Saueressig built a purpose-made calendering machine for continuous electrode coating with micron precision over the whole width of the web. *Why is this so important?*

No matter what the theoretical energy density of the electrode materials, the actual real-world performance of the cells is governed by the manufacturing process.

Calendering does two things. Firstly, compressing the coated electrode foil improves the contact between the particles of the electrode and optimises electron transfer due to lower volume



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resistance and reduced generation of heat.

Secondly, the smoothing of the surface that results allows more foil winds to be accommodated within a given diameter. In other words, it increases the power density of the battery being manufactured.

Being able to deliver accurate compression over the width of a surface being embossed, coated or laminated is a clear fundamental in Saueressig's engineering knowhow, which has been transferred to the battery making process. Saueressig has designed their roller technology so that the rollers can be flexed to deliver more pressure at particular points across the foil.

Since developing their first calendering machine, the company has gone on to develop a process more suited to needs of electrode foils designed for large format cells. Very important for the production of large format cells, where the coating is not continuous, is the patented gap system enabling thickness accuracy of +/- 1um regardless of the kind of coating.

The new gap control system is designed for mass production and has already been delivered to Germany's Bosch, Evonik Litarion, Karlsruhe Institute of Technology and Institute for Particle Technology.

In addition, Saueressig has developed 'pilot scale' calendering machines for laboratories or fledgling lithium-ion producers not yet ready for full-scale production. In all, Saueressig has delivered 14 production lines and several laboratory lines.

Saueressig's exposure to the exciting world of battery development has helped them develop calendering lines for dry blend films — in essence calendering fine powders into membranous materials which can be wound — the key technology needed for making supercapacitors and more.

Whether this will be the limit of the company's foray into battery toolmaking remains to be seen but one thing is certain: it will be an innovative and creative partner to serve the battery industry with tailor-made equipment. International battery manufacturers at Battery Japan will be in for a surprise in the array of production line equipment they can now buy from Germany.



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Picking up good formation

It is the formation of lead-acid batteries which turns lead compounds into positive and negative electrode. Our resident lead-acid master craftsman Mike McDonagh explains the formation processes for flooded batteries and their effect on plate structures.

The ability of the lead-acid battery to provide a voltage and current is due to the chemical structure of the positive and negative electrodes. It is the difference in potential between the positive plate (PbO₂) and the negative plate (Pb) in dilute sulphuric acid that creates the lead-acid battery.

In previous articles we have discussed the processing conditions that create an active mass to maximise the lead-acid battery's performance. It is the formation process that will now turn these complex lead compounds into electrochemical machines, capable of storing and providing electrical energy.

This process is so called because this is the first time the material has been converted into electrodes. In other words this is the process that forms the positive and negative electrodes, which is the basis of the secondary lead-acid battery. The initial stage of formation is the filling of the dry unformed battery with dilute sulphuric acid.

This stage of the process is important and if not controlled it can cause detrimental side effects including the formation of a passivation layer on the conducting substrate (PCL effect). For this reason the process of acid filling and soaking of the plates in dilute sulphuric acid will be treated as a separate process.

In this article the formation

processes for flooded batteries and their effect on the plate structures will be examined. The previous articles have concentrated on adjusting process parameters in order to end up with the structures and chemistry appropriate for particular applications.

The formation process is the last opportunity to ensure that the structures obtained from the previous processes will be converted into suitable and appropriate active material with the best possible properties for the battery application. The parameters and conditions necessary for the successful conversion for both 3BS and 4BS dry cured paste masses for flooded batteries using pasted plates will be reviewed for both positive active material (NAM).

This will form the basis for understanding how to provide the processing conditions and formation algorithms that are required to ensure maximum battery performance and process efficiency.

Formation chemistry

The basis of all batteries is to create a potential difference between plates immersed in electrolyte. This basically means a different state of energy to allow electrons to flow from one plate to another until both plates have similar chemical energies, much like two containers with different amounts of water in each joined by a valve.

When the valve opens the



potential energy in the higher level causes the water to flow into the second container until the levels (and therefore the potential energies) are the same. In the case of the lead-acid battery we have to create that imbalance by forming two different chemical species for the positive and the negative plate, i.e. PbO₂ for the positive and Pb for the negative.

Before formation, both plates have similar chemistry, mainly lead oxides and sulphates, so when immersed in dilute sulphuric acid, there is almost no voltage and no energy difference to create an electron flow when the plates are connected. Once a current is applied, the polarity is chosen to ensure that the electron flow is in the right direction to pump electrons from the positive into the negative plate.

Since most of the lead compounds in the active mass are the divalent form, when two additional electrons are removed by application of an electric current, the resulting tetravalent lead ions require four electrons to achieve chemical stability. Two oxygen molecules provide the required number of electrons, whilst the two electrons transferred to the negative

plate fill the electron vacancies in the divalent lead ions of the active mass, i.e. PbO_2 is formed in the positive and Pb at the negative.

Pb2+- 2e = Pb4+Lead- 2e^- = Lead dioxide(sulphates,monoxide etc)

Pb²⁺ + 2e = Pb Lead + 2e = Pure lead (sulphates, monoxide etc)

It is evident from previous articles that the actual structure and the chemistry of the dry cured paste is complex. The dry cured structure, before acid filling, will have an effect on the properties and performance of both the PAM and NAM.

However, the basic reactions and the electrical energy required for conversion can be illustrated with reasonable simplicity if we take the plate chemistry after soaking in sulphuric acid. If the sulphate from the acid is used as the divalent chemical species we can give the following as a simplified description of the conversion of the paste mass into electrochemically active battery electrodes.

Positive:

 $PbSO_4 + H_2O =$ $PbO_2 + H_2SO_4 + 2e^{-} + 2H^{+}$

Negative: $PbSO_4 + 2e^2 + 2H^+ =$ Pb + H SO

 $Pb + H_2SO_4$

The general overall reaction can be simplified to the classic chargedischarge reaction of the double sulphate theory.

 $2PbSO_4 + 2H_2O =$ $PbO_2 + Pb + H_2SO_4$ (reversible)

It is important to note that the production of sulphuric acid is

a by-product as the formation reaction proceeds. This is important as the kinetics of the reaction and its efficiency can be impeded by concentration effects. This will be discussed in the next article where optimisation of the various formation methods is examined.

The theoretical quantity of electrical energy required for formation can be simply calculated by using the Faraday constant (96 500 coulombs) that will liberate one gram equivalent. This is in ampere-seconds. To obtain this in ampere-hours (Ah) divide by 3 600 which is 26.8 Ah. Technically this is for one electron mole and, as we all know, a coulomb is one amp for one second and one amp is the charge of 6.241x10¹⁸ (Avagadro's number x 10¹⁸).

As this represents one electron per atom, we need to multiply by the number of electrons involved in the reaction or the valency of the material. In this case we are dealing with a divalent state and so there are 2 electrons not one that are passing per second. So for one kilo of lead formed from the dry cured paste in the negative and positive respectively, we have: 2 x 26.8 x 1000/207 = 258.94 Ah/kg of lead in the active material.

The amount of lead per kg of dry cured active material can be calculated from knowledge of the chemical species in the dry cured paste. Most companies have different paste formulations and different free lead, PbO and sulphate content. Based on these paste formulations, the theoretical quantity of electrical energy can be calculated.

If Ah/kg of dry cured active material is required then the value of 26 800 Ah should be divided by the weight of dry cured paste that contains one kilogramme of lead in both positive and negative plates. In view of this it is best for the reader to calculate the mass of the dry cured active material that results from one kilogramme of lead in the positive and negative plates.

These values are theoretical and clearly a lot less than the values normally used for charging lead-acid batteries. Aside from the simplistic model of chemical equivalents we have to consider efficiencies.

This is where the real world has a nasty habit of reminding us that the second law of thermodynamics has a big brother and his name is Murphy. As we know every possible obstacle which nature can summon in order to make life harder for technicians and engineers can and will be used to this end.

These obstacles will be discussed in the next article, along with their origins and the operating conditions that will minimise their effect. These are the structure and shape of the active material; polarisation effects on the electrodes; secondary reactions creating heat and unwanted by-products' morphology and crystal structure of the active material; current collector and active material interface' current density during charging; specific gravity (SG) of the sulphuric acid.

These factors have to be considered in order to arrive at a process which is optimised to give minimum time, maximum conversion rate and appropriate properties to the finished battery.

The physical and chemical structure of the dry cured paste and how they are affected by the formation reactions are now considered.

Acid filling and soaking

This process is considered separately as it plays an important role in determining the acid access into the active material and the formation of lead compounds on the active material/conducting

Table 1 – Comparison of acid filling parameters for different processes and applications

| Process | Acid SG | Soak time | Maximum temperature | Battery types |
|--|---------|---------------|------------------------|--|
| Tank plate formation (all battery types) | 1.05 | 1 – 2 hours | 45C | All |
| Container formation single shot (automotive) | 1.240 | 0.5 – 2 hours | 55C | Automotive, semi traction, monobloc |
| Container formation two shot (automotive) | 1.15 | 0.5 – 2 hours | 55C | Automotive, monobloc |
| 2V Container formation (tubular pickled plate) | 1.15 | 1 – 2 hours | 65C | 2V traction cells |
| 2V Container formation (flat plate standby power) | 1,240 | 2-4 hours | 55C | Standby power, UPS |

cured paste. This generates heat and results in a temperature rise in the battery or formation tank.

The temperature continues to rise until the rate of the reactions slows to a level where the heat loss to the atmosphere of the system begins to override the internally generated heat of reaction. The maximum temperature reached depends upon the acid strength, the chemistry and the physical structure of the plates.

Although there is a difference between the 3BS and 4BS cured plates, in general, the conversion of the cured active mass to lead sulphate is restricted by the penetration of sulphuric acid into the particle. *Figure 1* shows the probable zonal structure of a dry cured pasted plate after soaking in dilute sulphuric acid.

The larger the particle the more time that is required for the acid to penetrate. Additionally, the larger the particle the lower the temperature rise due to a smaller surface area which reduces the rate of the reaction in the active mass. According to Professor Detchko Pavlov the following reactions occur during the soaking process:

1. $4PbO + SO_4^{2-} + H^+ = 3PbO.PbSO_4.H_2O$

- 2. $3Pb0.PbS0_4.H_20 + S0_4^{2-} + H^+ = 2(Pb0.PbS0_4) + 2H_20$
- 3. $PbO.PbSO_4 + SO_4^{2} + 2H^+ = 2PbSO_4 + H_2O$

4. $4PbO.PbSO_4 + 4SO_4^{2} + 8H^+ = 5PbSO_4 + 4H_2O$

All of the above reactions result in alkali conditions with a pH dependent upon the activity of the $SO_4^{2^2}$ ion.

The heat generated from these reactions increases the temperature and helps to improve the reaction rate. There is no definitive guideline as to the maximum or minimum temperature desirable but generally lower temperatures are favoured for cold cranking and automotive starter batteries, whilst higher temperatures are generally accepted for tubular and traction batteries.

The effect of soaking SG and soaking time on the properties of batteries has been studied. *Figure 2* shows the effect of three different SG values of sulphuric acid and the time of soaking.

It can be seen from **Figure 2** that an initial filling density and soak times of several hours would be beneficial to obtain the best balance of performance for automotive batteries. The SG of 1.15 is normally associated with

FIGURE 1 – Schematic representation of zonal processes in a lead acid battery plate after acid soaking



FIGURE 2 – Effect of filling acid density (1.05, 1.15, 1.25) and soaking time on initial capacity and cold crank performance Pavlov et al - JPS 1993



substrate interface. The strength of acid used, the temperature reached during the soaking process and the time of soaking are all critical factors to consider when deciding on the process conditions.

In the processes we are examining, there are three specific gravities of sulphuric acid used for the initial filling and soaking stage. **Table 1** shows the processes, the SG, and the soaking periods that are commonly used for flooded lead-acid batteries.

The soaking of the battery plates either in the battery/cell jar, or in open formation tanks is required in order to create uniform conditions throughout the active material structure. As the acid is added it reacts with the basic sulphates, oxides and free lead in the dry

two shot formation processes. The use of 1.06 SG acid for a two shot process would require longer soak times and not provide sufficient conversion of the cured paste to a reasonable sulphate content.

There is a difference for 3BS and 4BS cured pastes. This is predominantly in the crystal size and individual pore volume of the active mass. The 4BS crystals are larger and consequently provide larger pore sizes to be filled with acid. The reaction rate for 4BS crystals is slower than with 3BS due mostly to the reduced surface area.

The sulphation reaction progresses more slowly as the thickness of the lead sulphate layer on the surface of the 4BS crystal increases with time. The temperature rise of a 4BS structure is considerably less than that of a 3 BS structure.

The higher the temperature then obviously the faster the reaction rate. This reaction rate is further increased with temperature, more than would be expected by Fick's law. This is due to the increase of the porosity of the sulphate layer with temperature, allowing easier transport of $SO_4^{2^\circ}$ and H⁺ ions along with water to penetrate into the crystal. However, despite this, a 4BS cured plate will not achieve the level of sulphate conversion that will be afforded by a 3BS plate.

Electrochemical conversion of the cured active masses (formation) process

In general the process of forming the positive and negative electrodes can be regarded as having distinct stages. These stages are defined by the chemical, physical and electrical changes that occur within the active masses during the formation period. These stages are as follows:

• Formation of a bonded interface between the grid and active

material. For the positive this will be a corrosion layer and for the negative it will be a growth of metallic lead from the grid into the interconnected active mass;

- In the positive another layer forms on the corrosion layer. This is what Pavlov calls the Active Mass Collecting Layer (AMCL). For the negative plate, this stage is characterised by a rapidly growing zone of lead sulphate and pure lead that extends initially from the grid to the plate surface then grows inwards to the rest of the active mass. This forms the interconnecting lead structure which provides the current path for active material conversion;
- Conversion of the cured paste material into the positive and negative active masses. This is the part of the process in which the capacity of the battery is determined. It is also the period in which the voltage of the battery begins to rise more rapidly;
- Electrochemical decomposition of water. Once the battery voltage has risen above the threshold for evolution of oxygen and hydrogen, water is electrolysed and is lost as gas bubbles nucleating on the electrodes.

The conversion of the cured paste material into the active masses of the electrodes, as a function of percentage completion, is represented by *Figure 3*. This diagram also shows the changes in electrolyte density and temperature which can be expected over the formation period.

The changes to the active material and to the electrolyte will be influenced by the starting material and the method of FIGURE 3 – Formation progress vs theoretical capacity input, SLI batteries Bode – Lead acid Batteries 1977 formation. For example, a tubular plate battery will have a different composition in the unformed state from that of an automotive pasted plate. It will also depend on whether the plate had been acid dipped, slurry filled or dry filled.

The method of formation, either single or two shot in the battery container, or single plate formation in open tanks using dilute acid, will also influence the chemical and physical changes in the active material during formation. These processes, their application and optimisation, will be discussed in the next issue.

An important aspect of the formation process is the efficiency of the conversion. This has implications for the time of the process, the additional heat generated, the consequences of





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Punched Grid (Spiral Wound Battery)

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side reactions such as hydrogen evolution, the initial battery performance and the whole cost of the operation.

The effect of increasing formation times, for example, may result in additional capital equipment being required to meet output targets, or perhaps reduce outputs and therefore increase amortisation of equipment. Other factors, such as additional environmental controls and shelf life, are also considerations when designing the processes and equipment.

Taking the general equation for forming the positive and negative electrodes, it is evident that sulphuric acid is produced at both poles within the active masses during the conversion to lead and lead dioxide. However, at this stage it is necessary to consider the formation of the positive and negative plates separately.

The processes and efficiencies are different, the time taken and the percentage conversion to reach the formed state are imbalanced. Nevertheless, there is a general principal which can be applied to both electrodes and which can be used to demonstrate one of the causes of inefficiency in the process.

According to reactions 3 and 4 both electrodes will eject sulphate ions during the formation process to form sulphuric acid in the bulk solution. During this period the concentration of sulphuric acid at the plate interface and at the surface of each active material particle is increasing. The pores in the active material structure will also have a high level of sulphates.

This condition will shift the equilibrium in the reactions and suppress the rate of formation of the two electrodes. The concentration gradient effect is shown in **Figure 4**. FIGURE 4 – Concentration buildup of Sulphuric acid from the plates into the bulk solution



This profile is relevant as it demonstrates the barrier to the ejection of sulphate ions from the active mass to form sulphuric acid. The concentration gradient produced at the surface of the plates remains reasonably constant during application of the charge current.

However, the concentration of acid in the bulk of the electrolyte will rise which slows down the migration of the sulphuric acid molecules into the bulk solution. This concentration increase at the surface of the plates, in effect, raises the voltage and therefore the energy required for formation, as well as extending the time of the process. This concentration effect will be examined later when discussing methods of formation.

Other factors affecting the resultant formed active materials are the paste density, temperature of formation and the current density used. However, at this point it is relevant to consider the positive and negative plates separately.

Formation of positive plates

As outlined above there are four stages to the total formation process. The first is the establishment of a corrosion layer of PbO_2 at the conductor/ grid surface in contact with the sulphated, cured paste mass. After this process the positive active mass is formed and it has been shown to proceed in two stages.

In the first stage, H_2SO_4 and H_2O penetrate from the bulk of the solution into the plate. As a result of the chemical and electrochemical reactions PbO and basic lead sulphates are converted into αPbO_2 and $PbSO_4$. These form at the surface and gradually penetrate into the active mass crystals as described above.

During the second stage of formation $PbSO_4$ is oxidised to βPbO_2 . It is in this stage that sulphuric acid is formed and diffuses into the bulk electrolyte. The phase composition of the active mass can be illustrated by **Figure 5** that shows how the



components of the dry cured active mass alter over time during the positive plate formation process.

It is evident from this diagram that the formation of lead dioxide within the plate is still occurring after the theoretical charge levels have been reached. The progress of the conversion of the cured paste to the positive active mass (PAM) can be described in three basic steps:

- Formation of a conduction layer at the grid/active material interface;
- Growth of a skeletal αPbO₂ conducting layer throughout the active mass containing macropores;
- Formation of the βPbO₂ agglomerate structure, providing the bulk of the battery capacity.

The structure of the forming active mass is influenced by the original structure. In 4BS pastes, there are long needle-like structures which are preserved during formation and which become the α PbO₂ conducting network with the PAM structure. *Figure 6*, which is an SEM picture taken from work done by Pavlov in 2001, is a striking verification of this mechanism.

lon diffusion and migration are considered to be the rate-limiting steps of the processes.



FIGURE 5 – Formation progress vs theoretical capacity input, SLI batteries Bode – Lead Acid Batteries

FIGURE 6 - SEM

picture showing

cured 4 BS paste crystals - a) before formation and b)

PAM structure after

. Pavlov – JPS 2001

formation

From this, it is evident that a high concentration of sulphate ions and sulphuric acid molecules would inhibit the reactions forming lead dioxide. During the first formation stage, the direction of advance of (PbO₂ + PbSO₄) zones into the paste is determined by the degree of paste sulphation, formation current, temperature and phase composition of cured paste.

The formation of the two allotropic forms of lead dioxide is an important factor in determining the properties of the finished battery. The α and β forms have been shown to have different contributions to the performance of the positive plate.

The β modification, formed in the last stage of formation, appears to provide the bulk of the electricity during discharge, whilst the α form seems to provide a rigid interconnecting network of electron conducting material to the grid/AM interface. The effect of the α/β ratio on the battery performance will be discussed in a later section which will be describing the optimisation of the processes.

Formation of negative plates

As with the formation of the positive plate, formation of negative plates can be identified in four stages. In the first stage



there is an initial high resistance interface between the cured paste mass and the lead alloy conductor.

The surface structure, after soaking, consists mostly of Pb(OH) and PbO₂ crystals, with possibly PbSO₄ depending upon the soak time and the acid strength. This causes a high resistance layer, which in turn creates a high initial voltage as soon as the current is switched on. Once the interface areas in contact have been converted to a common material, (in this case Pb), the transformation of the sulphated dry cured paste to NAM commences. This process also has two distinct stages.

The first stage is the electrochemical reduction of PbO and basic lead sulphates to lead and sulphuric acid. During this time, a lead skeletal framework is formed. This consists of a network of bonded crystals of irregular shape with PbSO₄ crystals bonded onto the framework or skeleton surface. The SO₄²⁻ ions, produced from the reduction of the lead sulphate, help to produce the acidic conditions necessary for the deposition of lead rather than lead hydroxide into the structure. In this way, zones are formed on both plate surfaces before spreading into the interior of the plate.

The probable generalised chemical reactions are as follows:



From this it can be seen that lead, lead sulphate and water are produced, the H⁺ ions producing water are provided from the bulk electrolyte.

In the second stage, reduction of PbSO₄ to Pb occurs and lead crystals are deposited on the lead skeletal surface in a strongly acidic solution produced from the generation of sulphate ions as described above. It is during this phase that sulphuric acid is produced, the lead sulphate crystals on the surface of the Pb crystal network are reduced to Pb and water electrolysis creates hydrogen gas. From this point in the process, the negative plate contributes to the rise in electrolyte density and the gassing associated with the latter part of the formation cycle.

The lead sulphate produced by the first stage reactions will be reduced to lead which will provide sulphate ions to form sulphuric acid in the bulk electrolyte.



The provision of electrons to the negative plate from the formation current reduces the lead ions liberated from the lead sulphate to metallic lead. The electrolysis process breaks down water to create hydrogen, which is evolved as a gas on the negative plate.

Efficiency and process variables

There is a significantly lower conversion efficiency for the positive plate compared with the negative plate. This is partly due to an increase in voltage that promotes oxygen evolution in the early stages of formation, and partly due to the difference in conductivity of the two active masses.

Lead dioxide in the positive is a semiconductor that will not

be as effective as the pure lead matrix of the negative active mass. These factors increase the charge factor required to complete the formation process. A factor is used to multiply the theoretical energy requirement for formation to ensure that maximum conversion in a reasonable time with reasonable energy usage is achieved. This charge factor is also dependent upon process conditions, initial material composition and plate design.

There are several factors which have an influence on the efficiency of the process and also on the resulting structure and properties of the active masses. These factors also influence the performance characteristics of the battery, affecting cycle life as well as capacity and high rate discharge capabilities. The process variables considered are formation current density; temperature; electrolyte concentration; and total coulombic input.

There are different formation methods commonly in use for flooded lead-acid batteries, notably single shot container, two shot container, recirculating acid and open tank formation. The principal battery types examined are, 12V automotive, monobloc traction, 2V standby power and 2V tubular and flat plate industrial batteries.

In the next issue, the various processes currently in use will be discussed, along with recommendations for formation algorithms for different battery designs and applications. It will be demonstrated that by knowledge of the mechanisms described for the production of PAM and NAM in lead acid batteries, the formation process can be designed to not only reap the benefits realised by control of all the previous processes, but also to enhance the battery performance in the chosen market sectors. 🗘



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Everybody's gone supercaps, Supercaps USA

Peter Harrop of British electronics market intelligence firm IDTechEx reports from the Supercapacitors USA 2013 show, which took place in Santa Clara, California in November.

There is no substitute for getting out there. In recent weeks, myself and the IDTechEx team have visited supercapacitor manufacturers NEC Tokin, Nippon Chemi-Con and JSR Micro in Japan and interviewed many professors and manufacturers presenting and exhibiting at the Supercapacitors USA show, part of the Printed Electronics USA event, in Santa Clara, California.

Those touching on supercapacitors included Armor, Cabot, Cellergy, CapXX, Power Paper, Maxwell Technologies, Stevens Institute of Technology, Florida State University, Australia's University of Newcastle, Australian National University, the UK's University of Surrey, UC Davis, Chrysler Group, Robert Bosch, the US National Renewable Energy Laboratory and Visedo of Finland, with its large WIMA watercooled supercapacitors in giant construction vehicles.

Speaking on graphene in supercapacitors, possibly the end game for both AC and high energy density versions, were Graphenea, Graphene Frontiers, Graphene Devices, Graphene Technologies and Nanotek Instruments/Angstron Materials.

Replacement of lithium-ion traction batteries with supercapacitors in hybrid electric vehicles is now commonplace, but the opposite is not. The US National Renewable Energy Laboratory has successfully replaced the NiMH battery in a hybrid car with a supercapacitor storing less energy, while Toyota has a traction supercapacitor in the Yaris Hybrid-R concept car. Indeed, a Japanese supercapacitor distributor, claiming to be close to what is going on, told us he confidently expects batteries in the Toyota Prius will eventually be replaced with supercapacitors.

The safety, life and performance advantages of supercapacitors mean they will increasingly replace or at least partly replace rechargeable traction batteries in vehicles, even without coming anywhere near to the energy stored in those batteries replaced. That happened long ago with Automatic Guided Vehicles (AGVs), which are also recharged frequently, thus needing minimal energy storage and therefore energy density, cost per unit of energy stored not being the primary consideration.

Nonetheless, this is not a unanimous view for all types of hybrid vehicle. Certainly, designers of hybrid vehicles must now consider the supercapacitor option.

Cap-XX reminded us that many electronics applications also have low average power, but need bursts of high power, making



supercapacitors an ideal solution. Examples set out included wireless sensor networks (WSN) for HVAC control systems, motion detection for lighting controls/security systems, vibration for bridge monitoring/process machinery, GPS location tracking, retail distribution centre information displays and so on.

For these applications, batteries have limitations because cycle life is limited and failure is unpredictable. Moreover, maintenance, replacement and disposal are expensive; the operating temperature range is limited - especially at low temperature. High power plus high energy/long life may be incompatible goals.

Electrophoretic EP displays

Cap-XX said that lots of autonomously powered devices would benefit from a low power display including time, temperature, status in WSN/M2M devices like industrial controllers, thermostats, HVA and lights; e-Book readers, Electronic Shelf Labels; RFID tags, electronic forms, signature pads, PDAs & POS terminals; medical devices such as digital stethoscopes and blood pressure/heart rate monitors; and clocks & watches.

Replacing energy harvesting batteries

Energy-harvesting integrated circuits designed to charge supercapacitors have been released recently. Where a supercapacitor replaces the battery in energy harvesting, it buffers the load from source and vice versa, converting low and fluctuating power to stable voltage and peak power to the load.

The requirements here are that the average load power should be less than the average source power. The supercapacitor is at its best where the average power is much less than peak power. The source sees constant power load set at maximum power point and the load sees low impedance power supply for the required duration. They must behave gracefully into a short circuit, start charge from zero volts, provide over-voltage protection, prevent the supercapacitor discharging into the source and optimise efficiency.

Replacing batteries and tantalum capacitors in pulse applications

The Cellergy stand had an excellent demonstration of how their small laminar supercapacitors with aqueous electrolyte are replacing tantalum electrolytic capacitors or fairly large batteries for electronics. This is because of cost and performance benefit. However, although low ESR (equivalent series resistance) is part of the requirement here, they are not currently contemplating developing larger versions for replacing AC electrolytic power capacitors.

Replacing stop-start and conventional lead acid batteries in conventional vehicles

Maxwell Technologies and separately Nippon Chemi-Con







Wireless mesh network based on Linear Technologies/Dust Networks SmartMesh IP Motes + Cellergy super capacitor as energy storage.

have recently offered a single pack designed to replace both stop-start and regular lead-acid automotive batteries. The pack contains supercapacitors and a Cellergy supercapacitor in wireless sensor network node Photo by IDTechEx small battery and, as a result, lower cost and better performance are claimed. These combos are taken seriously in an industry in which some view lithium-ion batteries on their own is a loser for stop-start.

Amazing attractions of graphene

It is generally recognised that graphene supports near ultimate performance in all types of supercapacitor from high power and high energy density to micro-supercapacitors. It has the highest intrinsic capacitance density at 21 microfarads per square centimetre. This is based on 2670 square meters per gram and leading to 550 F/gram according to Angstron Materials although Graphenia said 200 F/gram. Plus, of course, it has remarkable conductance rivalled only by superconductors, so very low series resistance is in prospect.

Western enthusiasm

Graphenea noted that graphene patents have risen sharply. IDTechEx would add that this is a Western phenomenon. In 37 visits to electronics and electronics materials and processing companies in Japan in recent weeks, not one was enthusiastic about graphene. We found just one Japanese enthusiast at Printed Electronics USA. On the other hand, Europe and USA have hundreds of graphene research teams springing up and generous finance for such programs.

The co-owned Nanotek Instruments and Angstron Materials noted that graphene is conducive to the utilization of high-voltage electrolytes, (e.g. ionic liquids, 3.5-6.5 V), but this requires meso-scaled pores (2-10 nm). Currently only 20-30% of graphene area is active in

2500 -2000 -1500 -

graphene supercapacitors, we were told. Therefore, we need inhibiting re-stacking of graphene sheets.

3000

Professor Jim Zheng of Florida University warned that energy density of complete supercapacitors is limited by current electrolytes to no more than 7 Wh/kg due to ion count. However, new electrolytes help to increase energy density. Indeed, with Nanotek's electrolyte, 180 F/ gram is observed versus 166 with a commercial electrolyte, voltage rises from 2.7 to 3.3 volts.

Energy density rises from 6 to 13.6 Wh/kg.

We noted several manufacturers of symmetrical supercapacitors claimed something near the higher figure in the laboratory: some claim to match lead-acid and nickel cadmium at around 50 Wh/ kg. Commercial success will be boosted by good yield, low material cost, retaining long life as good power density. Pure graphene is extremely expensive but any narrowing of the gap with batteries on power density or with electrolytic capacitors on power density could trigger considerable new sales.

Graphene patents by material by year Source: US Patent Office, Graphenia

Graphene microsupercapacitor: where electrolytics cannot go

Graphene Devices' microsupercapacitor is a hybrid device licensing technology from Rice University. Graphene and carbon nanotubes (CNTs) are joined to utilize a high surface area of a CNT 'forest' to demonstrate what CEO Robert Anstey called "ground-breaking performance which allows us to charge portable electronics in seconds and the replacement of batteries".

Anstey added the micron scale size of these devices would integrate into modern electronics for AC line filtering and discrete power sources with reduced size and weight, and with a planar geometry to accommodate the trend for thinner products and incorporate into existing production techniques. Existing capacitor technologies such as the aluminium electrolytic capacitor scale down poorly in size and are not suited to planar geometries of most processes and technologies.

The bad news is that, for the foreseeable future, their costs are prohibitive, so commercial launch is not yet planned. However, as Graphenia pointed out, graphene is intrinsically cheap. Dr Linh Le of Stevens Institute of Technology spoke on "Inkjet-Printed Graphene for Micro-Supercapacitor", showing one route to cost reduction.

Graphene Frontiers has developed a hybrid of carbon nanotubes and graphene that prevents reagglomeration restricting the available surface area. Imaae shown is of hybrid carbon nanotubes/ graphene for supercapacitors by Graphene Frontiers Source: Granhene Frontiers

Inkjet-Printed Flexible Micro-Supercapacitor



Electrostatic charge
 separation at electrode electrolyte interface

 Higher specific power (~100x batteries)

- Rapid charge/discharge times
- Millions of charge/discharge cycles

In their assessment, graphitederived graphene will cost a mere \$50/kg within three years. In this context, graphene oxide is ink jet printed, then converted to graphene in-situ, micropatternable at 50-micron resolution. It is additive, netshape manufacturing with minimum nanomaterial use, handling and waste generation.

Scale-up and integration with rapidly emerging printed electronics is in prospect. Power and energy density are not impressive compared to today's larger commercial supercapacitors but making it very flexible, reelto-reel compatible is uniquely useful. Stevens Institute of Technology spin-off FlexTraPower will make it all happen and be in operation in January 2014.

Supercapacitors: Gaining traction in a world of batteries

The replacement of batteries means grabbing a chunk of the lithium-ion battery market in particular, but also inroads into lead-acid and nickel metal hydride territory. Lithium-ion batteries alone present a market five times that of aluminium electrolytic capacitors to go for, so replacing aluminium electrolytic capacitors that we touched on earlier will remain a minority sport. The same is true of tantalum electrolytics where the marker is even smaller.

It was therefore pleasing

to hear Dr. Priya Bendale of Maxwell Technologies talk on supercapacitors gaining traction in a "World of Batteries". In our opinion, Maxwell is the most creative marketer in the industry, opening up new applications all the time. Dr. Bendale focussed on transportation, notably heavy-duty vehicles and regenerative braking energy recovery, and combining supercapacitors and batteries for engine starting and start-stop for conventional vehicles.

Thanks to Maxwell, there are over 20 000 supercapacitor-based hybrid buses in use worldwide, some in use since 2002. They are the preferred solution because cycle life is 8-12 years, cold weather performance is excellent, weight is less, storage efficiency is better, there is simple monitoring and balancing and no thermal runaway failure modes.

Supercapacitors are needed for a reliable stop-start system because batteries are not efficient in receiving and delivering power at high rate, in cold weather, battery charge acceptance decreases and lead-acid AGM batteries 'cycle down' when not allowed to completely recharge in stop-start applications.

Nevertheless, supercapacitors are not yet the preferred solution, being outsold by lead-acid batteries at least three to one in this application, mainly because PbA is cheaper. Maxwell has Inkjet printed microsupercapacitor schematic Source: Stevens Institute of Technology sold over 600 000 stop-start supercapacitors for French car manufacturer PSA diesel hybrids and its competitors are racing to copy them.

Advantages of the PSA system include up to 15% fuel economy improvement in urban driving, reduced carbon dioxide emissions to comply with EU mandate, a 30% smaller battery, reduced cabling and assembly labour, extended battery life, 'every time' restarts in all conditions and voltage stabilization for the entire electrical system.

A good compromise is a battery with a supercapacitor across it, as with the Batscap in the Bollore pure electric car and the Nippon Chemi-Con one across the traction battery of the Mazda pure electric car. Maxwell has now offers a supercapacitor/lead-acid battery combination to replace the conventional vehicle's stop-start and starter/hotel facilities battery. In forklifts, a combo extends useful life between charges by 33%, we learned.

Increasingly, combos reduce cost up-front. One example is: 2000F +30 Ah motorcycle battery, total weight 13.6Kg – a 25% reduction. Higher minimum voltage, lower ESR, longer cycle life, protecting the battery and lower temperature operation are cited. A study by Argonne National Laboratory found that cycle-related battery capacity degradation decreased by a factor of two and cycle-related battery impedance degradation reduced by a factor of 5.9.

It is no longer contentious that supercapacitors across traction batteries increase vehicle range by up to 10%. It is bad news for the battery industry because its market is reduced in a double whammy: the battery can be smaller for the same range and it lasts longer. •



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Testing, testing: A gap in the market

Clean Horizon is a French energy storage consultancy, which in October 2013 signed an agreement to license battery performance data from the French Atomic Energy and Alternative Energies Commission (CEA) as part of a new service for energy storage project developers to choose the correct battery system. The Editor spoke to the founder and CEO Michael Salomon.

How does Clean Horizon earn its keep?

We are a consultancy specialising in grid-connected energy storage research. We offer three types of report: **'Detect'**, **'Analyse'** and **'Monetise'**.

When I founded Clean Horizon I was a contractor for a venture fund in the United States. I did a Ph.D. in aerospace. I moved back to France to work for McKinsey, but I found it very boring and left after a year.

Without external funding the company has grown fast with turnover growth of 50 to 60% every year for the past four years.

You recently launched 'StorageAudit' – a third-party battery auditing service. This is a big leap from producing mere market reports. What made you decide to offer this service as well?

You need to be sure of how the battery is going to age. The key in financing energy storage projects is to be able to independently audit how to size the system and how it will perform so that financiers can trust project developers, and invest.

At today's prices a 13-year life lithium-ion battery for frequency regulation application would have a just about acceptable IRR (internal rate of return) for investors of 8%,



but a nine-year life battery would offer and IRR of only 4%.

I started the company within a venture fund and I speak to the investment community. An investor always needs to conduct due diligence. To do this requires a third party, i.e. a consultant, to verify the assessment.

A French investor wanting to invest in an energy storage project on a French island using a, say, A123 lithium battery there is no-one.

In 2012, I was speaking with stakeholders in the US who were telling me, "Look, we need a service to help us to size energy storage projects because we as integrators need to know which battery vendors to work with and thus convince our project developer clients that we are correctly sizing their projects."

The project developers have the same problem as us – they have no way to check whether what is being sold to them is fair and accurate. A project developer needs this not only to select its battery partner but also to convince its customer. Upon returning to Paris, I thought this a very valid point.

How can a third-party audit batteries without a test lab?

I contacted the CEA. It took us a long time to figure out the best way to bring the service together. An organisation such as CEA is not really set up to offer this type of commercial service, they are very much about scientific research.

We had to come up with a way to structure a partnership which could leverage their IP to deliver the value required by the market.

We signed the agreement in October 2013. We initially started working with CEA in 2011 when they bought one of our market reports. CEA bought of our Analyse reports in 2011 and bought another in 2012.

Right now it is a licensing agreement but perhaps later on



Usage parameter 1

Usage parameter 2

the nature and structure of the partnership may change.

Why the CEA?

They have peer-reviewed, laboratory-verified models for how cells and batteries systems age. In conjunction with INES (Institut National de l'Énergie Solaire), CEA has conducted a five-year study into electrochemical energy storage.

In so doing, INES-CEA has accumulated "extremely vast" field knowledge and modelling of how different batteries and different battery chemistries age in a variety of real-life storage applications, such as frequency regulation, over long periods.

CEA produces a great deal of battery performance data and they want to continue testing batteries into the future, in fact, due to our association they may expand their research into new batteries.

We want to use this IP to create battery models to answer the questions of financiers and project developers, which for the latter is essentially can you help me correctly and independently size my battery. In order to remain credible, I need them to continue their research - practically every year the battery manufacturers launch a new cell or module.

Knowing how French industry can sometimes operate, is this a ruse to sell French cells and battery packs, like those of Saft?

They are not just French cells. At this stage, I don't want to be in the pay of certain battery manufacturers, or be a new sales channel for Saft. In fact, Saft is not even one of our customers. At this stage, I want to remain neutral.

Personally I cannot tell you which come from South Korea or China or Japan or the United States. There are not many French lithium-ion manufacturers!

CEA has tested 75 different lithium cells from 45 manufacturers. CEA has also tested approximately 10 lead-acid cells, some flow batteries and a flywheel.

Compared to other research laboratories, this is a lot. Before we signed the partnership I researched what other labs around the world have done, particularly in the United States. I could not find such an extensive volume Figure 1 Lifetime of a battery system subject to real European frequency following different usage scenarios of data anywhere else, not even Sandia National Laboratories.

How extensive is the testing?

Not all the test results have been transformed into models. The difficult part turning the data into a model, this is two months work. It is not clear if all them have been modelled because the key is to testing to make battery aging models. I don't know exactly how many have been modelled.

Also, I could not say which lithium cells are the best or the worst because I do not have access to the data. Furthermore, nobody at CEA has access to all the data either. Most the data is 'anonymised' in terms of the manufacturer.

How do you go about testing cells at the CEA?

If you are a battery manufacturer and you want a test, the CEA will conduct the test and send the data back to the manufacturer. They'll send you a test report and also how you position your cell within the other cloud of datapoints they have tested.

The other 'clouds' of data points are 'anonymised'. They keep track of which system does what but I'm not aware of who is behind each data point and I' m not sure that there is one engineer who knows the name of the manufacturer behind each data point.

What is the end-result of a 'StorageAudit'?

There are two key competences. The first is to be able to accurately model the function of the batteries, the second is to be a energy storage system sizing service provider with a quick turnaround.

What we want to work towards is to be able to tell our clients, "Look. Given your specific scenario, we believe the cheapest solution based on our price assumption

should be 2 MWh of LSP-type batteries." That is our service. I am not going to tell them you should buy 2 MWh of BYD, Saft or A123 batteries. This is what we want to get into, and I think it will take some time to achieve it.

How long will a 'StorageAudit' take to conduct?

We can do assessments now but for the 'error bar', and I think the error bar is key, will take four to five months. The error bar is the margin of error of, for example, using a 2 MWh LSP battery for a certain application on the lifetime of the storage system.

If I know I have 12 ageing models for LSP batteries, then I am confident in our estimate of the performance of a 2 MWh battery with an margin of error of +/- 'x'%. So this means we can say to our clients you should use a LSP battery of 2 MWh +/- 'x'%, which would give you an internal rate of return of 8% +/- 'y'%.

The margin of error is key for insurance companies and investors. But right now we don't yet have enough models in the database to define an adequate margin of error. It will take us another for five months to get there.

Why bother with a thirdparty audit when battery manufacturers like Samsung SDI offer 20-year warranties?

In theory, project developers and integrators don't need our input. Standing in the shoes of a hopefully honest and conscientious battery manufacturer, he will also say you need a 2 MWh battery, +/- 1%. I can say that because I know my battery inside-out, I made it and I have tested it for years.

Figure 2 Profile and

rules

power a PV plant

island following

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Even if that is true and the customer believes me, I am still going to need a 10 or 15-year warranty. The issue is when a thirdparty developer tries to finance the project, there is no reason for him to trust my performance estimation.

The financier will probably trust my warranty because Samsung is a very large company, but how does the banker know that Samsung provided the most conservative estimate when sizing the system appropriately and not maximising their sale?

It is like a match without a referee - or, indeed, the referee is one of the players. This is unsatisfactory in the long term. In the beginning, our customers will probably be buyers of energy storage, perhaps smaller utilities or project developers which don't have the resources of, say, EDF with thousands of engineers to run models. Smaller customers clearly have no way of checking.

Even in the case where there is a long warranty offered by the battery manufacturer, the project investor needs someone to talk to. But there's no one out there. For companies that don't have the balance sheets of, say, Samsung, this is a real problem.

Will CEA test batteries to order?

If CEA has not tested a particular cell requested by a project developer then we cannot help them. They will test batteries to order in the future. If a developer approaches me with an idea storage with, for example, an iron-chromium flow battery by EnerVault which CEA has yet to test then I'm stuck as we have no models. The best I can do right now is to offer something approximate, which is unsatisfactory.

What CEA has as part of their remit is to keep on researching batteries. So they could call EnerVault and ask them, "Do you guys want to be part of our testing programme for a small fee?" Then the two could strike a deal where the battery company sells a system to CEA, CEA tests it and sends back the test results plus all the other services to help them situate themselves against all of the other batteries.

By definition this will take some time to develop, especially for testing battery ageing.

If a project developer calls me tomorrow and asks me to size a project with a new untested battery within a four-week period, I am stuck. This is why I created a partnership with a lab like CEA, which has an extensive database. From what I have seen they have the most extensive database.

What is your likely customer base?

The first customers are likely to be small project developers, in particular for solar PV. They will have no interface with CEA, which has no desire to sell the service itself.

We are expecting to sell the service to system integrators we will market the service to the storage community.

We may even sell the service to storage vendors, but that I was not expecting. This was a surprise to me, I was not expecting this type





of approach of showing which technologies are best. This will probably be transient.

The goal is not to provide yet another service to the storage community, it's ultimately a service for the financial community so they have someone other to talk to about the technology other than the vendors.

What is the benefit of 'StorageAudit to the CEA?

Every time we activate their IP we pay them a fee. For CEA, it's a way to monetise their research.

Their IP is really to do with batteries. They have developed an optimiser software program called M2C. They created in-house to be able to size battery storage systems correctly for specific applications and that is the software we are using and going to be updating on a regular basis. A co-updating arrangement.

Technically the software does not care which energy storage application is inputted, be it wind, solar, frequency regulation or anything else. I'm training some of my team to be able to exploit CEA's IP and their proprietary software to optimise storage sizing.

CEA is a huge organisation with 16,000 researchers, 95% of them involved with nuclear power. It is not an organisation short of funding but all the same they could have charged a higher rate for the IP.

The energy storage laboratory team at CEA are proactive and positive, they understand we are a start-up and they also understand we cannot come to an agreement which significantly increases their workload. We are not going to add to their burden on a daily basis, we merely wish to use their IP and pay them for doing so.

Will you work only with CEA, or are you exploring other options to verify battery performance?

So far we are the only working with CEA in this way but I cannot say it is an exclusive arrangement.

The CEA battery lab is in the Alps in a city called Chambery. We work with the CEA team at INES, the French National Institute for Solar Energy. Analysis of the profitability of a 1 MWp PV asset following French regulator requirements depending on battery size and efficiency

Figure 3

INES was created by the CEA though technically it is not owned by them. It is a mixed research group with local universities.

It is a huge site and every time I visit I discover a new warehouse! They test solar PV with energy storage using four real-size houses.

They have 250 channels to test cells, it's a huge facility.

Have you received much interest in 'StorageAudit'?

Right now we are at the proposal stage. We are in discussions with three prospects, one in the United States, for solar PV, and two in Europe, one for frequency regulation. None in France! The other European prospect wants us to model the performance of a new technology in various energy storage applications versus the performance of incumbent technologies in the same applications.

We need to spend more time and resources on this project and it will take time. I founded Clean Horizon in 2009, we have no venture or government funding, we have to take it step-bystep. Possibly we may apply for government funding in the future, but not in the short term.

If the partnership with the CEA works we will look to strengthen the partnership and take it to the next level. We are looking at this as a project to grow the business further. If it does what I want it to do I may look to leverage. We need to increase the sales power.

The energy storage market will really take off when there are independent third-party auditors of battery technology so that bankers can be sure of performance and lifetime. This expertise will lead battery suppliers to offer 'real' long-term warranties and thus lower financing and overall system costs. •

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India's battery industry hits a roadblock on economic woes

South Asian correspondent Dipak Sen Chaudhari laments India's long road to economic recovery and the knock-on impact for the sale of batteries in the world's third largest economy.

The great Indian economic success story is over – or is it a passing phase? The double-digit growths of 2003-2009 was abruptly halted, as it was in many nations. Even the most optimistic pundit estimates the declining trend will continue and India will do well if growth hits 5% in 2013/14.

While this is largely attributed to the wavering policies of central government, it cannot be denied that it has much to do with the general myopia vision of India's corporations in going for short-term gains without investing in technology to ensure long-term stability.

The storage battery industry, almost entirely lead-acid, is no exception and the current year is one of their worst years yet. The pull from both automobile sector and other industrial sectors have severely slackened, with almost every manufacturer suffering from huge over-capacity. As a consequence, there is a price war amongst the big manufacturers, while many of the smaller one are on the brink of calling it a day.

Domestic sales of the automobile industry registered a 3% growth, for the period April-September 2013, the first six months of the current financial year. However, this growth is mostly due to substantial improvement of sales of low-cost two-wheelers.

During the same period



passenger car sales declined by 4.6% and that of commercial vehicles by as much as 16% year on year. The sharp decline of the overall economy is reflected by a 26% drop in sales of light, medium and heavy commercial vehicles.

As for exports, even though there is an apparent improvement of sales by 5.4%, the sale of commercial vehicles has fallen by 14.6%. Passenger cars and twowheelers exports have seen a very healthy growth of 13.5%, though again this may be due to the marked weakening of the rupee against the dollar.

The Indian car industry has not had it so bad since the mid-1930s. This has had direct impact on Indian battery makers, almost all of whom had planned major expansion to their manufacturing capacity in the past 3-5 years. Now that these have been installed and ready to churn out millions of batteries, suddenly the demand seems to have gone for a toss.

India's sluggish economic performance has taken a very heavy toll her other industrial segments. Telecoms, which experienced explosive growth in the first decade of the millennium, is almost comatose.

A series of scams involving the top brass of the telecoms companies and government officials, including political leaders, have been a total dampener. The absence of any real industrial growth, together with the government's ambivalence towards allowing large international retail companies setting up shop in the country, has meant very poor growth in the motive power too.

The UPS industry has slowed down as most Indian companies go slow on their computerisation and associated activities. Neither does there seem to be much hope in the immediate future for the storage battery industry in this prevailing scenario.

One of the biggest paradoxes is that India has been able to bring down her net power deficit sharply, previously one of the major negative talking points of the Indian economy. Even though the current installed capacity of power generation (thermal, hydro, nuclear and non-conventional), is 229 GW, the actual availability has always barely been half.

In September 2012 power demand was 132 GW, while average generation was only 118 GW – a deficit of 11%. Last September, demand rose slightly to 134 GW, but availability reached 129 GW – leaving a deficient of comparitively modest 2.7%.

With electricity utilities set to add a plethora of new power stations in the coming years the major issue of India being a powerstarved nation may slowly become a thing of the past. There are still, however, major issues of power transmission and distribution across the vast hinterlands,

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meaning there will still be power outages'of varying lengths in the rural and semi-rural parts in the years ahead.

This scenario leaves the Indian battery industry with a major problem. The increasing gap between power generation and demand and consequential power outages developed a major industry helped develop a major industry known as the domesticinverter or home-UPS segment.

Almost every Indian home and small office, one must say grudgingly, had to buy a home-UPS together with a large lead-acid battery as back-up almost as inevitably as one would have a fan, a refrigerator or an air-conditioner. The inverter and battery industry is huge - at least \$1bn of batteries alone were sold in 2012/13.

This year, with the significant improvement of the power situation, together with a relatively mild summer, there is a sharp drop in demand. No manufacturer is prepared to give the actual figures, and it can only be estimated that the sales of batteries from this segment have declined by at least 20% in the past year.

The situation looks grim. With almost every segment of battery users looking to be on the downward slope, it is time for battery industries to tighten their belt and wait for this phase to get over.

Later this year India will hold a general election and it

is hoped whichever party wins and forms the government will take a robust decision to put the industry back on track. The battery industry, however, is not a primary industry and it will have to wait for the return to health of the big infrastructure companies telecoms, automobiles and others— before they can see a reversal of their fortunes.

Meanwhile, there is an opportunity for individual battery manufacturers to review closely their own operations, cut down on waste, improve operational efficiency and bring in better technology so that they will be ready, far leaner and fit, to take up the growth challenges as soon as they come. •





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Cryogenic energy storage: Running the gauntlet

Many great energy storage ideas never make it to market. Can Highview Power Storage cross the valley of death to commercialisation? Ruth Williams visits the pilot site in the English town of Slough to find out if they can make the progression from pilot to production.

ighview Power Storage (HPS) has been working since 2005 to develop cryogenic energy storage and now is it crunch time. The British company was founded by Peter Dearman, the engineer who developed cryogenic energy storage, along with Toby Peters and Ferd Burger.

Cryogenic energy storage is an umbrella term for liquefied air energy storage, a technology that HPS is the first company to develop. Initial research was carried out at the University of Leeds, followed by lab tests then

the pilot plant in Slough, which has been running successfully since 2011. The next step is to demonstrate a larger site that will draw in customers and ensure



The liquid-air tank at Highview's pilot plant in Slough, UK HPS does not fall into the black hole of failed great ideas.

The pilot site, measuring 600m², contains all the equipment to turn ambient air into energy for storage. Using a method of repeatedly compressing and cooling air, liquefied air is stored in a cold store then re-heated as required, put through a turbine, into a generator and the resultant electricity can be used on-site or returned to the electricity grid.

The pilot site can provide 350 kW of power and has 2.5 MWh of energy storage. This has been enough to prove the theory, but liquefied air storage is fully scalable from 4 MW/16 MWh, up to 100 MW/1000 MWh.

The liquefied air system works by taking ambient air from the surroundings into the first compressor; it is compressed to nine bar before being stripped of moisture, carbon dioxide and hydrocarbons that would hamper the heat exchange process in the cold storage tank.

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The high-pressured gas enters another compressor that raises the pressure again up to 13 bar then the highly pressured air is sent to the cold storage where it is progressively cooled using a liquefaction cycle,



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Nick Castellucci, senior mechanical engineer, explains the similarity with electrochemical storage systems: "There is a charging device, which is the hydrogen plant; a storage device which is the cold tank; and a discharge device, which is the turbine." The 'charging device' is an air liquefaction plant that performs a series of compression and expansion cycles that cools the air to the point that it liquefies, which is approximately -170°C.

Castellucci explains liquefaction could be performed at any pressure to suit a site set-up. He says the pilot site ran on a low-pressure cycle. "Although it is not as efficient as a higher pressure cycle, we had limited funds available, so had to go for lower. We just wanted this site to prove it is possible to store liquid air in a tank and use liquid air to generate electricity and this tank does that."

The liquid air is stored at around -170°C in an insulated tank at low pressure until it is required. This can be five to seven days before it would need to re-processed. When power is required liquid air is drawn from the tank and pumped to high pressure and heat is applied.

The system can capture waste heat from any industrial site such as a data centre or metal processing plant. The pilot site is adjacent to a power station so the steam is harnessed to warm the liquefied gas with a heat exchanger from -170°C up to +70°C. This results in a phase change from liquid air to high-pressure gas, which is in turn used to drive a turbine and generator.

This power recovery stage involves the cold exhaust being removed using a refrigeration unit in the cold store, the re-captured cold can be reused in the liquefaction process.

The entire set-up uses standard gas works equipment, with compressors and liquefaction equipment that could be procured from any supplier. Although liquid air has not been processed in this way before, liquid nitrogen is very commonly processed and stored so the equipment is widely available.

Although the set-up looks fairly complex with pipes and tanks feeding into one another, Castellucci swears the process is simple and efficient.

The recycling of waste heat demonstrates the flexibility of the system. It has the potential to be used in conjunction with an industrial site as energy storage, or an additional source of revenue using familiar equipment that can be synched with the existing site.

HPS's site in Slough has simply been a testing ground that has served its purpose and is now not in regular use. HPS has plans Nick Castellucci, Highview's senior mechanical enaineer to build a scaled up version for proving the technology works at utility scale, the next site will be ten times the size of the pilot. This is essential for the future of the company, as it will act a shop window showcasing the technology. The location has not been decided upon yet; it depends on funding, as is so often the case for pre-commercial projects.

HPS is aiming the liquid air system at utility customers installing storage at grid-level. Gareth Brett, CEO of HPS, explains the business model: "It is different from other storage technologies because we are not manufacturing anything. We provide the engineering design, process design, help a customer procure the equipment and get a contract in place with a contractor to build one of our devices. The design would be by HPS, but the customer would effectively purchase it from the engineering, procurement and construction (EPC) contractor. "Our business model involves engineering services around the design at the front end of the process and some licencing around the technology use – so it is effectively an IP and engineering services business," he added.

HPS's business plan is selling the details of the system including engineering know-how and configuring the machinery together to work as a cryogenic energy storage system. This makes it difficult to offer a price for the system or predict an average return on investment (ROI), Brett says with the relevant financial details from a customer that a ROI can be given, "It's all about what their energy costs are and what time of day they use power at and what the drivers are for the revenue streams the device might be able to generate." Castellucci believes customers will be reassured by buying familiar equipment from

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reputable suppliers to lessen the investment risk.

The cost of a plant will depend entirely on size of set up. But Castellucci stresses the key selling point is its flexibility of set-up, scalability, the familiarity of equipment and lifetime of 25 years plus.

At storage level, the system has been designed to work at grid-level and would fit into any industrial location. Scaling up from the compact footprint of the pilot (25m x 25m) would involve extra storage tanks for cryogenic fluid, but the overall size would be comparable to a large battery installation, but with greater energy density.

This puts a cryogenic system somewhere between batteries and pumped hydro. "In terms of economics, it's bulk energy storage as opposed to fast acting shorter duration storage," says Brett. "We're not competing with batteries; we're trying to do something different. We have more storage in the tank but it doesn't react quite as quickly. It is for longer-term reserve type of services."

Castellucci says the cryogenic system could be attractive to a range of users: "There are lots of key markets but our first targets would be in the utility sector, but also to end users such as steel mills, gas power plants – anywhere with waste heat could be a key market," he says.

The attraction for network operators with a system over 20 MW may be the strongest, as Brett adds: "Between 20 – 50 MW with around 200 MWh of stored energy the costs become more attractive, that puts you at the large end of the distribution network or small end of distribution." This would include network operators and integrated utilities that cover network operation to generation. The other group being targeted is large-scale industrialists running energy intensive processes such as petrochemicals, metals production etc.; any process that requires a large amount of energy but also creates waste heat that could be captured. Integrating a liquid air system with existing industrial processes means the customer can take advantage of demand side management using its own stores of energy.

Actualising the next demonstration site is down to funding, which may come from any number of sources. The UK's Department of Energy and Climate Change (DECC) has been running an energy storage competition since October 2012, HPS has been whittled down to the final 12, in November 2013 Moixa and REDT were announced as winners and HPS is also expected to get a share of the £17m (\$27m) kitty but no official announcement has been made.

The results of the DECC funding could allow HPS to scale up to a site that utility customers are keen to see.

Brett says he doesn't foresee any problems with scaling up the technology - rather that scaling it down was more of a challenge because the tanks and compressors are manufactured for larger gas installations.

But if no funding comes from DECC, there are other sources of



The 'cold store' energy storage tank on top of a container housing the generator and turbine in Slough,

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revenue to be explored. The EU's Horizon 2020 programme offers funding for low carbon projects that HPS would be eligible for; a partnership with German gas supplier Messer group makes HPS entitled to funding from the regional German government to set up a demonstration site in Germany.

As for the UK, it is not primed for energy storage at the moment says Castellucci. "Here in the UK there is no market, customers on the generation side and demand side are not interested because there is no incentive or market for it at the moment." Wind farms are currently being paid for curtailing their output at high generation times so there is no incentive for using storage in conjunction with the wind. However with gains being made for energy storage in many other countries, HPS are confident there is room in the energy storage market for this size contender. Germany's Energiewende has resulted in surplus renewable generation at time so storage integrated to the grid is being installed as part of the ambitious plan to move away from fossil fuels; California's Public Utilities Committee has mandated the installation of 1.325GW of energy storage by 2020.

The UK is playing catch-up and still has a long way to go, until then there are a lot of other markets HPS can tap into around the world, Castellucci says they have interested parties from Brazil, China, South Africa, USA and Germany. The team is confident that a utility-size demo plant will convince even conservative buyers of its worth. As with any large projects, nothing will happen over night and buyers are cautious of novel technologies. The notion of liquid air is becoming more prominent and as industry becomes more familiar with the concept future projects will be easier to develop.

Following two years at a pilot site now is the time to turn a proven idea into a workable business. HPS has reached the point where it is aware of its own mortality, having a proven theory is all well and good, but selling a system from the next project is essential to the survival of the business as it runs the gauntlet between pilot and commercialisation. •

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A flaming nuisance

Gerry Woolf sits in on an automotive battery safety meeting in Germany. As the auto industry gears up to launch a range of top dollar EVs and hybrids, too much faith is placed in the humble nail for testing purposes.

Battery fires don't just get headlines: they cost you money. With images of a blazing Tesla Sedan still etched in our collective retinas, you can only wonder how Elon Musk felt as the stock price of his company slipped away as mainstream media all over the world 'gilded the lily' on Tesla's piece of bad luck.

Gasoline-powered cars burst into flames every day— in accidents and spontaneously, killing hundreds of people every year. But electric cars must behave as newly-arrived immigrants to a hostile host nation— being exemplary in every way. Should just one break the law, the wrath of the host nation comes down on the innocent as well as the guilty.

And at IQPC's two-day battery safety summit in the German city of Wiesbaden in December, the great and the good of the German car industry reflected on what they were doing to ensure their latest models of both cars and batteries aren't beset with the same headlines that punched a hole in Tesla's stock price.

So, what can possibly go wrong to cause a fire? As if we didn't know! Overcharge, heat, short-circuits of the spontaneous and the inflicted kind, like the Tesla 'event'.

It's easy to tell auto engineers struggle with the chemical aspects of all of this. There is, after all a lot to take on board.

Kai Christen Moller, of the Fraunhofer Electrochemical Institute, whom I've quoted in these pages before, does his absolute best.

"A battery is a compromise of reluctant properties," he says. It certainly is. A material a fraction of the width of a human hair is all that is between effective operation and a short-circuit.

Electrolytes based on organic solvents with low boiling points and flash points. Cathodes sensitive to heat and which can decompose and add more available oxygen to a fire. Anodes which have the potential to allow lithium metal to plate-out and burn.

Lithium-ion is a technology with known risks. The auto engineering community looks to standards to minimise these risks and a comprehensive set of defence measures to protect against



failure at every level— cell, battery module, system and automobile with comprehensive testing to validate everything. Whether that's enough will be evident in the next couple of years.

Armin Warm of Ford Research Europe directed the meeting to the key pieces of legislation laid down by the European Union which govern this: UN ECE100.02. This governs the testing of the battery system and came into force in July 2013.

They are certainly comprehensive taking in the following: thermal shock and cycling; mechanical shock; mechanical integrity; fire resistance; external short circuit protection; overcharge protection; over-discharge protection; and over-temperature protection.

And these are not the only rules



What can possibly go wrong?

Lithium-ion:

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that govern batteries. Lithium batteries have to meet safe transportation criteria governed by UN38.3 testing.

This stipulates that each lithium cell and battery type must have been successfully tested to provide evidence of transport safety prior to any shipment. The shipper must be aware that the cell, battery or the battery fitted to a vehicle has been successfully tested.

Furthermore, batteries have to be manufactured in accordance with a quality management programme. But the rules also state the defective cells and batteries destined for teardown or recycling cannot be transported by air— this creates special problems for auto makers who are made to ship packs considerable distances for further investigation.

Warm explained that Ford has already developed a protocol to handle potentially defective batteries, whereby the packs get opened and use is made of a Midtronics discharger which de-energizes the battery at a rate of 7.5A. The batteries can then be shipped in special crates for further examination. Other OEMs are likely to have to adopt similar procedures.

The argument of who takes responsibility for safety systems cell maker, pack maker or auto OEM has been much debated in these pages.

A123, now Chinese-owned, showed the eloquence of its battery pack design, which incorporated a textbook layered defence strategy, from cell through to module and battery pack, culminating in an interface with the vehicle.

A123 is the battery supplier for the Chevy Spark, the budget priced EV version of what was originally something horrible from Daewoo and sells in the UK for less than £7 000 (\$11 500) in a gasoline version.

Each cell has a circuit board for current, voltage and

temperature sensing with CAN bus communications to the battery control module. There are individual current sensing modules and an electrical distribution module, which ties together the various packs distributed within the vehicle. It is this module that interfaces with the car.

The packs are 'armed' with contactors, which are set 'open' and the BMS checks the health of the system before applying power to the vehicle's electrics. If the BMS fails, the battery modules can be cut out by an independent piece of hardware.

Finally there is old-fashioned fusing at cell, module and pack level for further electrical safety.

Too bad that just 400 vehicles have been sold in the US prior to its 2014 launch.

The defensive layered approach

Ubiquitous nail tests can be made 'easier' appears to be somewhat universal. Dr. Olaf Bose of SK Continental described much the same idea with slightly different terminology. At the cell level SK has adopted the soft pack design, which is less prone to gas formation than a hard prismatic cell case.

Much of the meeting however became embroiled in the philosophy of safe design with few revealing as much of their hand as A123 did. Two young men from Jaguar and AVL Land Rover showed much to define the nature of battery hazards, dividing the risks into thermal chemical electrical and kinetic, but showed nothing as to how the risks were mitigated in practical designs.

Perhaps the most worrying presentation of all came in the field of cell testing.

Michael Danzer of ZSW presented a paper co-authored by Harry Doring. This author's heart sank - we're back to discussing the simulation of internal short circuits through the use of nail puncture tests.

Tests that can be easily tailored so that cells will pass.

It seems the work of Brian Barnett and Tiax has not travelled to Europe, but the extensive studies we've reported in BEST demonstrate that puncture tests do not really represent internal short circuits. At best they represent what might happen in some kind of abuse situation, such as the crushing or penetration of batteries.

It's well understood that internal shorts come about through either dendritic growth or contamination of battery electrodes— or is it?

That's a good question. Perhaps in Germany it is not so well understood. The auto engineers have their standards and their EU regulations. Legislation established,

Legislation established, therefore closed thinking? Let's hope not. •

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Next-gen materials make EV dream a distinct possibility

BEST's resident lithium-ion specialist Rick Howard goes beyond the products specs of today's materials and looks down the pipe to high voltage cathodes and graphitic anodes that really maker forecasters dreams come true.

here's a lot of hot air and 'finger in the wind' estimates about the electric vehicle markets and the future of lithium-ion battery demand. When it comes to cars the arguments boil down very simply.

Today's Li-ion batteries have both limited mileage and high price tags: what is the industry developing to meet these challenges?

The short answer is highcapacity cathode materials with low cobalt content coupled with non-graphitic anodes with superior lithium storage capability. Why low cobalt? Because this strategic metal is the most expensive component of a Li-ion cell, and with continuous pressure from automakers to reduce costs, it is obvious why LCO replacement is a primary goal. Metal prices are roughly \$20/lb (34.5€/kg) for Co, which is historically quite low, versus \$10/lb (17€/kg) for Ni, and the Co market is volatile while Ni prices are steady.

Further, based on a recent study from Brodd J. (Power Sources 231, 293 (2013)), materials cost for an LCO cell would be roughly \$2.00, with LCO accounting for \$1.20; replacing LCO with L333 NMC would reduce the base cost to \$1.30. Emerging oxide cathode materials contain as little as 10% Co, compared to 60% in LCO, and may also include significant portions



of Mn, about half the cost of Ni: this cost structure is obviously a major driver toward next-generation technology.

Energy generation

Electrochemically, the Li-ion cathode is where the action is: it supplies energy, while anodes simply store lithium. But conventional cathode materials, such as $LiCO_2$, $LiMn_2O_4$, $LiNi_{0.15}Co_{0.8}Al_{0.05}O_2$ (NCA), $LiFePO_4$, and the stoichiometric NMC family ($LiNi_xMn_xCo_{1-2x}O_2$), simply do not have enough capacity (energy) for long-range EVs, unless the vehicle is overloaded with cells or over-engineered for low weight and streamlining, both expensive propositions.

The current cathode energy density limits are roughly 700 mWh/g (gravimetric) and 1600 mWh/cc (volumetric), adequate for reasonably-sized modules powering commuter trips and local deliveries, but not enough for getaway weekends. Yes, additional energy can be extracted from these intercalants (except for LFP) by raising the charge threshold above 4.2V, but this creates a safety issue – the risk of O_2 loss into a hot cell with fuel (electrolyte solvents), potentially resulting in an "event," an industry weasel word for cell combustion and possible detonation.

There has long been a multi-

pronged research focus on boosting cathode capacity, which culminated (so far) several years ago with the discovery of high-voltage lithiated mixed-metal oxides (Dahn and Thackeray, among others). These species are described as layered-layered or layered-spinel composites, featuring LiMO₂ or LiMn₂O₄ moieties intertwined with Li₂MnO₂. Selective combinations of Mn, Ni, and (usually) Co exhibit >250 mAh/g capacity with an average discharge exceeding 4V, producing >1000 mWh/g energy, a 50% improvement over today's materials.

The weakness of such intercalants shows up at high voltages and above ambient temperatures, when they are prone to lose oxygen: this promotes a structural change resulting in spinel formation (from Li₂MnO₃), which causes the voltage profile to decay (*figure 1*). The result is an energy loss that can quickly be substantial under stressful conditions (*circa* 10% in less than 50 cycles, from the example above).

Understandably, manufacturers are unwilling to spend significant development money on EV batteries exhibiting noticeable energy declines after only a few months of daily use. Researchers are investigating the inclusion of stabilising admetals, such as Ti, Fe, or Cu in low concentrations, that will retard oxygen loss and



Figure 1 Voltage decay of the title laveredlavered cathode intercalant during cycling. Energy loss is approximately 45 mWh/g after 20 cycles, roughly o.22%/cycle or 3X the 'normal' loss due to capacity fade and resistance effects. Burrell et al. Argonne National Lab, at DoE Annual Merit Review, 2013

capacity of 277.3 mAh/g, capacity retention was 91.2% after 80 cycles, and power capacities were 141.5 mAh/g at 3C and 190 mAh/g after 100 cycles at 1C. Analyses indicated CaF₂ coating allowed an accelerated phase transformation from layered to spinel phase and suppressed electrolyte decomposition.

Finally, lanthanide oxide coatings work well in reducing Mn leaching from LMO (E-One Moli Energy patent) and lowering the charge transfer resistance during high voltage operations of layered-layered cathode species. The latter effect, coupled with a stabilised surface, was observed in $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$ covered with a 2.5nm shell of Sm_2O_3 , resulted in a discharge capacity of 214.6 mAh/g (91.5% retention) after 80 cycles between 2.0 and 4.8V. Conclusion: coatings will be necessary for electrolyte protection and long working life of emerging high voltage cathode materials.

A variation on this theme showed that coating the cathode, rather than the individual particles, could be even more beneficial to cell performance. A research team from the University of Western Ontario examined the effects of TiO_2 , ZrO_2 , and Al_2O_3 on both LCO particles and electrodes, and found the cell electrochemistry benefited more from CVD-coated cathodes. Further, improvements were dependent on the coating oxide: Al₂O₃ resulted in the longest cycle life, while ZrO₂ led to the highest power output. The implication is that some coating materials are functionally specific, and matching these protective oxides to particular intercalants may be dependent on intended cell usage.

EVs and HEVs that need acceleration for safe operation require power-type batteries. Such units are strong candidates for electrode nanomaterials capable

secure the Li_2MnO_3 component. This effort is still in the laboratory: immediate success would not be commercialised before 2016.

High energy cathode materials charging at elevated voltage have a secondary impediment to success, an obstacle that scientists have already overcome. Delithiated metal oxides are strong oxidisers and will attack conventional organic carbonate electrolyte solvents: the degradation products mostly collect on the anode and render the surface electrolyte interphase (SEI) layer less ionically conductive, to the point of complete blockage (accelerated capacity fade) and cell shutdown.

Fortunately, a proven cure for this malaise is to coat the active particles with a thin (<10nm) layer of amorphous ceramic-like material. This film serves two purposes: it hides the oxidising metal oxide surface from the solvents, so they are not subjected to the destructive power of >4.5V during charging, and it enhances Li⁺ diffusion into the intercalant particles, thus boosting rate capability. Although the coating process is not onerous, protected materials are not yet widespread in commercial cells. Most common is doped and coated $LiCoO_2$, usually with TiO_2/MgO , enabling manufacturers to squeeze an extra 10 mAh/g or so out of the cathode by charging to 4.3V without sacrificing safety. A further few high-voltage examples will suffice.

The most common coating is Al_2O_3 , an inexpensive and easyto-work-with material. As little as 1 atomic% on 4.7V LMNO₄ substantially extends working life for this notoriously short-lived power cathode. Capacity retention at room temperature and 0.5C rate improved from 64.4% (pristine LMNO₄) to 76.6% after 100 cycles. Even more dramatic was the performance at 55°C – a 1% Al_2O_3 veneer caused retention to jump from 22.4% to 78.5%.

Similar results were observed with 5 wt% Al_2O_3 -coated layeredlayered $Li_{1.20}Ni_{0.16}Co_{0.09}Mn_{0.55}O_2$ cycled at 50°C. Inorganic fluorides are also effective: CaF_2 -coated $Li_{1.20}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ exhibited markedly improved performance over the bare NCM material. First-cycle coulombic efficiency went to 89.6% with a discharge

of rapid discharge and charge, and as an added bonus, nanoparticles also increase working capacity, meaning longer runtimes: HEVs, for example, could nearly double their battery ranges with highperformance electrodes containing nanomaterials. Fast-charging capability is another plus for longdistance travelers, although not the strongest selling point: even in the US, typical use patterns provide for 30-60 minutes (or more commonly, overnight) recharging.

One last topic to be considered in the choice of next-generation cathode materials is the environmental impact of millions (or even billions) of vehicular Li-ion cells. A recent study (www.epa.gov/ dfe/pubs/projects/lbnp/final-liion-battery-lca-report.pdf) by Abt Associates, backed by government, industry, and academic groups, compared three contemporary Li-ion cathode chemistries used in EVs/HEVs. The objective was to identify major contributors to potential environmental and health hazards in the materials or processes from the entire battery life. The three materials were LiMn₂O₄, LiFePO₄, and $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$ (NCM 424): the first two are more suited to power assist in HEVs, while high-energy NCM is preferred for EVs, although cell performance was not a criterion for this study.

There are few surprising findings in this unique 128-page report, but the overall conclusions are eye-opening and well supported by the data. For example, cobalt and especially nickel are health hazards, and therefore NCM rated significantly higher in non-cancer and cancer toxicity impact potential than LFP and LMO. Production of Li-ion cathode materials is a known energy hog, but NCM requires up to 50% greater energy input, due to higher calcining temperatures and more complex processing. Having down-played NCMs, it must be noted that recycling or reclaiming Ni/Co substantially reduces the material's overall impact on the environment, because mining and processing of ores are energy-intensive and polluting activities.

The working life of a battery is an important vector in determining relative impact: a 2000-cycle-life cell with LFP has roughly half the effect from manufacturing as 1000-cycle spinel or NCM units. This will substantially lower the potentials for global warming, acidification, ozone depletion, and photochemical oxidation (smog) with LFP. Because EV batteries will likely incorporate NCM, they receive a lower environmental grade than HEV batteries. The exceptions with lower impact are global warming potential, abiotic (non-living physical and chemical attributes) depletion potential, and eutrophication (excessive inorganic nutrients in water) potential.

Abt authors presented several opportunities for emerging Li-ion battery technologies that would mitigate negative impacts on environment and health. The first two, commented on above, are extended cell cycle life and reduced proportions of Co and Ni in the cathode. These steps would also have the effect of significantly reducing battery energy costs for the consumer.

A not-so-obvious improvement would be a reduction in a battery's passive metal content (cell casing, pack housing, and battery management and cooling systems). Further, the use of reclaimed metals from the cathode, as well as optimisation of the cathode materials' processing, would lower manufacturing energy requirements. Finally, the reduction or elimination of solvents in battery production would lower costs and improve air and water qualities.

Lithium storage

Development of Li-ion anode materials beyond iterative graphite improvements was lagging until circa 5 years ago, with the recognition that extended cell run-time from higher capacity species could not be totally dependent on the cathode. Further activity was triggered by the emergence of the afore mentioned high-energy, high-power cathode materials that yearned for anodes with enhanced Li storage capability. The benchmark is, of course, graphite, and competing materials have to meet or beat the following standards: 340 mAh/g (270 mAh/cc) gravimetric (volumetric) capacity, <10% irreversible capacity loss during the formation (first) cycle, coulombic efficiency >99.8%, potential relative to Li⁺/Li^o <0.5V, and minimal capacity fade for hundreds, if not thousands, of cycles. Research into materials that might meet these criteria has accelerated, and scores of contenders (and pretenders) are described in recent scientific literature.

The supposedly low-hanging fruit in next-generation anode materials are elements that alloy with Li, led by Si, Sn, and perhaps Ge. Not so easily harvestable are species that will reversibly accept Li by intercalation or displacement; these incorporate multi-valent metals in ceramic-like compounds that are chemically reduced, allowing lithium storage. In bulk (micron-sized) particles, all such possibilities suffer a similar fate: they undergo high (15-60%) irreversible capacity loss during the formation charge-discharge cycle, and rapid capacity fade thereafter. The origins of this rot are electrochemically inactive crystal phases and lattice imperfections that irreversibly acquire Li after insertion (low Coulombic efficiency) and expansion/contraction-

induced fragmentation during lithium exchanges that cause sub-particles to lose contact with the electrode's conductive network, thus slowing Li⁺ diffusion.

Performance improves with nano-sizing: examples include Ni₃Si₂/Si nanorod arrays with >2000mAh/g storage capacity that lose >12% of their capability during the formation cycle. Somewhat better is Si nanoparticles dispersed in a Si-Ti-Ni ternary alloy, with 1100mAh/g capacity and greater than 90% first-cycle efficiency, but fade is a steady (and deadly) 2%/cycle. In theory, these alloy matrices offer the benefits of high conductivity, restricted Si expansion, and reduced reactivity toward electrolytes, but the production cost of such nanomaterials is far too high for commercialisation in the foreseeable future.

Two recent BEST Li-ion articles. on next-generation battery chemistries and anode materials, mentioned an exciting development opportunity: the concept of graphene covered with nanoislets of species that reversibly store lithium. In the initial paper, I speculated that high capacity decorated graphene might appear in commercial cells within a few years, certainly by 2020. I'm happy to report that I underestimated the industry: XG Sciences announced in April the availability of Si-decorated graphene anodes providing an unusually high Li storage capacity, and SiNode Systems is in advanced development of a related composite. These advances bode well for both power and energy capabilities, and may lead to the shot in the arm so badly needed by the automotive companies (and politicians) flogging electric and hybrid vehicles.

What is it about graphene that makes it such an exciting prospect for Li-ion anodes? Concisely



described as a one-atom thick layer of graphite, high-purity graphene is possibly the strongest known material, pound for pound, nearly transparent, and an extraordinary conductor of electricity and heat (and also the most hyped discovery in recent memory). Although physicochemical attributes were first calculated in 1947, it was thought that graphene could not be isolated, until 2003, when Geim and Novoselov at the University of Manchester (UK) prepared the material by the simple method of using adhesive tape to peel layers from a clamped piece of graphite. Their insight was rewarded when in 2010 they received the Nobel Prize in physics, and there is now an entire department at the university, dubbed Manchester Energy, dedicated to graphene research. After the breakthrough was published in 2004, global investigation into graphene exploded: in 2007, over 750 scientific publications appeared, and by 2010, that number exceeded 3200. Applications in electronics and chemistry are now discovered almost daily, especially graphene composites that exhibit synergistic properties with vast commercial applications.

The 3-dimensional detail

Figure 2 High resolution TEM image of single-layer graphene. Holes have approximately 2Å diameter. From Petronomist.com, 24 Feb 2013

Figure 3 Silver nanoparticles uniformly dispersed on graphene. From Zainy et al., Materials Letters 89, 180 (2012)





XG Sciences, a Michigan company producing graphene nanoplatelets by a hydrothermal process, entered the Li-ion market with graphene-silicon (G-Si) composites. I interviewed Rob Privette (Vice President, Energy Markets), who stated XG has sampled G-Si globally, with positive feedback from Li-ion cell manufacturers. The company offers "standard" materials. described as "short stacks of graphene sheets," with increasing Si loading, supplying 600-2000 mAh/g capacity. Exhibiting a density of 0.85 g/cc (slightly less than graphite but still competitive), these decorated graphenes

have volumetric capacities of 500-1,700 mAh/cc, respectively, 50-200% better than the best graphite. Privette stated that XG's composites with lower Si content have longer cycle life and are aimed at the portable electronic market, while the higher capacity G-Si materials are best suited for EV batteries. Further, Si loading can be tailored to the customers' needs: G-Si preparation is based on XG's proven graphene process, adding Si to the production stream without significant engineering changes.

In a press release, XG cited life test results of low irreversible capacity loss (10-15%) during the formation cycle coupled with minor capacity fade, in keeping with the concept that graphene stabilises decorative particles during cell operation. Of course, these attributes are dependent on the cell's working environment and electrode formulations. An additional plus: XG's unmodified graphene (*figure 4*) is suitable as an electrode conductive aid, boosting cell rate capabilities.

Privette was definitely bullish on the scale-up of G-Si, stating there is a very clear path to highvolume output. Information from XG's website (www.xgsciences. com) details current graphene production at 100s of kg per week, and the company is accepting 100 ton annual orders, with pricing below \$100/kg. An impressive start, although volume must



Fiaure 4

SEM photos of XG Science's graphene

nanoplatelets

Typical Agglomeration

significantly increase and pricing retreat to meet the marketing targets of automotive battery producers. Finally, Privette believes (as do most industry executives) in continued rapid growth in Li-ion technology, augmented by the development of high energy cathode materials and high voltage electrolytes.

A supporting instance of highperforming anode material similar to XG Sciences' is a Co₃O₄-graphene composite reported by Zhu et al. (J. Matl. Chem. 2013, 1(44), 14023). In this work, high density 2-3nm Co₃O₄ was introduced into fewlayered graphene: spectroscopic investigation revealed the oxide nanoparticles preferentially attached to defect sites on the graphene planes. This reduced irreversible Li entrapment on the graphene and therefore enhanced cycle1 coulombic efficiency. The very short Li diffusion distance into the oxide, coupled with easy electrolyte access and high graphene conductivity, allowed unusually high capacity and rate capability. Although the theoretical capacity of Co_3O_4 is 890 mAh/g, Zhu's composite achieved 1543 mAh/g at roughly C/6 rate and 1075 mAh/g at about 1.1C, with low fade. Similar systems with larger oxide particles produced only 1150 mAh/g, with >0.5% fade/cycle, affirming that smaller crystallites are more resilient during cell operation.



Edge View - Two

Other R&D teams are developing related anode materials, building on graphene's ability to enhance conductivity as much as 100X, which dramatically improves Li-ion cells' energy and power capabilities. Two early-stage companies, CalBattery and Vorbeck Materials, are working on graphene composites with very high power ratings. The CalBattery G-Si material is undergoing evaluation by Quallion as part of a government-funded development project for satellite use applications, and CalBattery expects their composite will appear in EV batteries within 2 years.

Other examples of emerging composites include MoS₂ nanosheets interleaved between graphene, yielding >500 mAh/g of stable Li storage capacity even at >2.5C; the nanosheets alone rapidly deteriorated, and MoS2 powder is an anodic disaster. A tin-decorated graphene, structurally similar to XG Sciences' short stacks, delivered 466 mAh/g reversible capacity at 1C after >4000 cycles; tin alone fragments and loses all capacity in a few score cycles.

A word of caution, however: as in art, too much decoration is unsuccessful. Single-crystal SnO₂ nanosheets were successfully deposited on graphene and achieved 975 mAh/g reversible capacity, but the first-cycle efficiency was only 71%, indicating an unacceptably high amount of lithium retained by the composite. In contrast, a homogeneous dispersion of 3-6 nm SnO2 nanodots on graphene flakes provided >550 mAh/g Li storage with <1/4 the capacity fade. (See figure 5 for decorative schematics.) Scientific journals abound with similar reports, limited only by the ability of the decorative species to reversibly absorb Li.

Cathode materials can also benefit from augmentation



by graphene templates: a team from Xiangtan University first coated LiMn₂O₄ (spinel) microspheroids with Y_2O_3 , then wrapped the particles with graphene nanosheets. The graphene/Y₂O₃/LMO hybrid had an initial discharge capacity of 129.3 mAh/g (usual is around 110 mAh/g), and capacity retention was 89.3% after 500 cycles at 1C rate and 55°C, conditions strenuous enough to devastate unprotected spinel. Further, the composite had excellent power capability, producing 90.0 mAh/g with 30C (2 minute) discharge. The lanthanide oxide coating suppressed Mn³⁺ dissolution, thus extending cycle life, and the graphene enhanced cathode conductivity, allowing improved rate (power) performance.

A Canadian firm, Grafoid, has invented a mild process yielding single-layer graphene. Because Grafoid limits itself to natural graphite products, it seeks partners for joint development of graphenebased materials, preferably at their northern Quebec facility next to their high-purity graphite mine.

Haydale, a UK firm, has patented a material-friendly plasma technology claimed to be scalable and capable of producing high quality graphenes that can be tailored to customer specifications. Another company, Graphene Frontiers, has developed equipment that allows continuous spray-deposition production of single-layer graphene at atmospheric pressure. A University of Pennsylvania spinoff, Graphene Frontiers avoids the expensive high-vacuum CVD process sometimes used for graphene production: their methodology is depicted in *figure 6*.

Commercialisation in the biosensor arena is predicted within two years, but for the moment, decorating these graphene sheets for energy storage applications is seen as too expensive to pursue. Partnering with an electrode manufacturer might facilitate this technology

Figure 5 Representation of various decorations on araphene. including nanodots (top left), nanoribbons (top right), and molecular species (bottom). Larger groups (bottom right) have less-than-ideal morphology, as they may fragment during cycling. From Chang and Wu, Energy Environ. Sci., 2013, 6, 3483

into the battery arena, with the objective of a binder-free anode.

There is some confusion over what exactly constitutes graphene. While Geim and Novoselov described it as a planar moiety with single-atom thickness, a more liberal definition today allows up to 10 carbon layers in a graphene particle. Electrochemical test results clearly show that short stacks of graphene, to use XG Sciences' term, have performances superior to conventional graphite. Modest mathematical calculations prove that decorated carbon species contain greater percentages of Li storage ingredient as the number of stack layers decreases. It must be noted that graphene composites are not limited to decorations on planar surfaces: structural variables can include wrapped, contained, and/ or sandwiched anode materials, and still display significant improvements in their energy and power ratings while enjoying extended cycle life.

Unfortunately, processing methods yielding modified graphene are typically complex and therefore pricey, making scale-up to commercial volumes a difficult venture. Creating flakes, usually by hydrothermal or chemical exfoliation, is a simpler



Graphene Frontier's schematic for continuous graphene formation on Cu foil

Figure 6

task than producing sheets: the former employs more "standard" equipment with greater output, although large-area graphene has better value-added prospects. From an economic perspective, the ultimate trade-off with competing anode materials will likely be the high process cost versus enhanced energy and power from singlethickness graphene composites.

A few researchers are taking graphene to a more esoteric level by doping the material with nitrogen or boron, then evaluating the electrochemical capability of undecorated flakes. This modification is accomplished by adding ammonium or borohydride species to the reaction feedstocks, and product performance is impressive. Reversible capacities exceeding 1000 mAh/g have been achieved at lower discharge rates, while *circa* 200 mAh/g (N-doped) and 235 mAh/g (B-doped) were obtained at 120C, with complete recharge and minimal capacity fade. Doping graphene produces a disordered surface morphology (resulting in better electrode/ electrolyte wettability and preferred bonding sites for functionalisation), increased intersheet separation (faster Li⁺ diffusion), and improved intrinsic electrical conductivity. Although results are impressive, this technology wrinkle is several years away from production levels.

A related approach that shows promise is to employ templates of various metal carbides and nitrides, which exhibit stable two-dimensional crystallinity. These materials, dubbed MXenes by Gogotsi and Barsoum at Drexel University, initially contain an A-group element (i.e., Si, Al, In,...) that is removed by acid etching under ambient conditions. Over 60 of these 2-D species have been isolated: they appear relatively easy to prepare and sustain without reassembly, boding well for manufacturing costs, and are hydrophilic, allowing facile dispersion in aqueous slurries. Like graphene, these Ångstrom-thin sheets produce longer anode working life, lower irreversible capacity loss during the first cycle, and better rate capability; unfortunately, commercialisation is still in the planning stage.

One final bite at the apple for the future of graphene in EVs: supercapacitors. Researchers at the Gwangju Institute of Science and Technology (Korea) prepared an extremely high surface area graphene that absorbs great volumes of an ionic liquid electrolyte. The amount of electrolyte determines performance: capacitance was measured at >150 Farads/gram, with energy storage of 64 Wh/kg, within striking distance of the 100-200 Wh/kg from Li-ion cells.

Supercaps are known for sterling rate capability, and this configuration is no different: charge was completed in just 16 seconds, and the prototype endured *circa* 10,000 charge/discharge cycles without significant loss of capacity. The obvious application for this technology is in EVs/HEVs with regenerative braking, and the inventors believe their high-energy supercaps will reach manufacturing volumes in the near future.

Conclusions

Industry analysts Navigant Research and McKinsey & Co. place current lithium-ion costs at \$500-600/kWh, and confidently anticipate process and material advances will drive prices down to \$180-200/kWh by 2020. But will that be sufficient to promote wide-spread adoption of EVs? Katherine Tweed, in a November 2013 GreenTech Grid article, makes the case that pure EVs will be little more than commuter cars until fast-charge stations have a substantially greater presence than they have now – about 3% of 12,000+ public chargers. These expensive level 3 stations can top off cells in 30-60 minutes, whereas low-cost level 2 chargers require at least 4 hours replenishing the battery electrons. Bottom line: EV appeal will be limited until owners can plan on 200-mile (325-km) trips lasting a reasonable 4 hours instead of an 8-hour marathon, and sales will fail to meet even modest industry projections.

Next-generation Li-ion electrode materials could go a long way in accelerating EV acceptance, and while the enhanced performances described above are by no means guaranteed, betting against technological advancement is a sure money-loser. High-voltage cathode materials producing energy in excess of 1 Wh/g already exist, and would be the answer to range anxiety. Stabilising these intercalants' structures with dopants to prevent voltage slippage and maintain long runtime between charges, nanosizing particles to improve rate capability (acceleration) and reduce charge time, and coating with amorphous ceramic-like species to boost rate performance and mitigate electrolyte decomposition, are the obvious development targets.

Decorated graphenes (or their ilk) portend similar advances for the anode: Li storage capacity increasing up to fourfold with the possibility of 2-minute cell charging, and electrochemical stability sufficient for several thousands of cycles. These next-generation electrode materials are not simply laboratory curiosities but are fast ripening into commercial development, and combined with the hoped-for proliferation of high voltage/high current level 3 rechargers, hugely optimistic predictions of explosive EV use within 10 years are not so extravagant after all. 🗘



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Pester power: Those who shout loudest get the cream?

Anthony Price, director of the UK Electricity Storage Network, opines on how the electrical energy storage industry should take heart from recent developments in the electricity sector and boast about its benefits to win favour.

Many of us are familiar with the way that children use every trick in the book to gain attention and demand something, and how they keep doing so until they eventually get it. A well-placed demand, repeated, can become wearing, but when repeated with well-made arguments, it can present logic, which makes it a natural conclusion that the protagonist gets what they want.

Our energy infrastructure represents an amalgam of concepts, some have been well planned, some arise because of a particular requirement– perhaps strategic or emergency in nature– and some because of the power of persuasion.

Who persuaded Britain's nationalised electricity industry to adopt nuclear power? It would be hard to believe that the decision was not taken without at least one nuclear champion extolling the virtues of a virtually novel technology to sceptical colleagues. Probably a liberal dose of pester power.



The 'merry-goround' coal trains revolutionised energy storage of a different kind

The power industry is not just about electricity. Large power stations needed large quantities of coal, and integrating coal trains with power stations needed considerable lateral thinking.

Collieries were built with miles of railway sidings, often full of rakes of small coal trucks. The sidings were used as much for storage of coal trucks as well as for storage of coal. As coal is electricity waiting to happen, this is a tale of storage familiar to many readers of this magazine.

It was a brave man, in the middle of the 1960s who persuaded British Railways, the National Coal Board, the Central Electricity Generating Board and South of Scotland Electricity Board to adopt the untried 'merry-go-round' trains. But the effect was significant.

Coal trains could unload without stopping; locomotives did not need



to be shunted from one end of the rake of trucks to another. Efficiency was up, costs were down, safety was improved, power stations became bigger and productivity rose.

Like small children trying out new games, the pioneers of the wind industry took their ideas and turned them into demonstrations, not really understanding the full implications of their actions, but certain that they had a better way of doing things.

These early developers knew they were doing something right, and being told to stop only made them more convinced to carry on. And carry on they did.

The power of pestering, at first to the utility companies such as



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California's PG&E, and later most of the companies across the world, made the advocates of wind power increasingly determined to make sure that everyone knew that wind was a clean and green technology, that it held a solution to providing low-cost, sustainable energy and that others were going to have to move their ideas, if not their assets, if they were to still have a place in their new world.

More recently, we have seen the power of persuasion from the solar industry. PV panels, once a novelty, are now common place. Support for all kinds of renewables is requested, and often granted. Pester power has paid off.

So where is the pester power from the electricity storage community? It's very easy to produce a list of reasons why electricity storage does not make the impact it should have in today's world – but we do need to be positive about being negative.

Pick up any report from the past twenty years and the reports generally say much the same thing. But has our pestering become worse? The reasoning behind our arguments should now be stronger. The basic theories of storage remain practically as constant as the laws of thermodynamics.

For anyone who has just started thinking about electrical energy storage please consider a few basic points. On most systems, the lowest initial capital cost for installing new generating capacity is a diesel genset or gas turbine. The running costs may be high, but

The powerful wind lobby has been remarkably successful. Can the energy storage industry achieve similar?



that is another story.

So, anyone considering doing anything that competes against a diesel or gas turbine has to make a very strong commercial case to gain a foothold in that market. But we do not have to give up.

The argument is simple: we should consider the whole life cost of the solution and the overall system benefit when making the case for storage. Putting a low-cost solution such as a diesel genset may solve a single problem in a quick way, but it may not be the best long-term solution.

So the electricity storage industry is right to keep making the point that storage can supply a whole system solution; it brings benefits across the value chain. So we also need to make the point that if there is a market for energy and ancillary services, it needs to be a proper market, with fair and undistorted access.

But this may not happen. The industry has been making this point for the past twenty or thirty years and change can be slow. Pestering because we have not got something, with a touch of jealousy is too negative.

Instead, let us look at the positive side of the industry. There are more and more good energy storage projects commissioned and in service, with many more in the planning and construction phases.

The US DOE database is rapidly filling with projects that are completed or underway. Japan is investing heavily in improving their national strength in key battery technologies such as vanadium flow and sodium sulphur.

South Korean industries are increasing production of lithium batteries; industries in China are not only producing and exporting batteries, but also installing substantial demonstrations to showcase their capability. The USA has a wide range of projects

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across the energy storage spectrum with a range of storage technologies from flywheels, flow batteries, conventional and advanced batteries as well as novel compressed air systems.

Meanwhile in Europe, there is a constant stream of new energy storage projects in Italy, Germany, Spain and the UK, to name but a few examples. The problem is not technology. The problem is not commercialisation, nor is it an understanding of the business structure for storage, in fact there probably is not a problem at allit's just that we have not argued strongly enough to make sure that we believe in storage ourselves. If we accept that storage is a viable way to make our power industry a little bit more sustainable, a little bit greener and a little bit more efficient, then the rest would follow.

The Electricity Storage Network, the UK's industry group for network connected electricity storage, is pressing the British Government to commit to four simple steps to develop electricity storage in the UK:

- a. To nominate an individual or section in DECC to have a specific responsibility to argue the case for electricity storage;
- b. To set a target for at least 2000 MW of new electricity storage by 2020;
- c. To create a new asset class with a separate licence condition for electricity storage;
- **d.** To develop and publish a strategy for electricity storage.

In Britain, these actions would reinforce the work already underway to support and nurture storage through the Low Carbon Network Fund, the DECC Innovation Competition, the Energy Systems Catapult for technology The 12MWe Regenesys flow battery at the Little Barford power station in Bedfordshire, UK. The unit was closed in 2004 by new owners RWE



development and the excellent work for supporting electricity storage research in the Universities and with Engineering and Physical Sciences Research Council funding. We just need to bring these all together.

No one doubts that the smart grid is the way forward. Every picture of the smart grid includes the need for electricity storage. Storage is quite clearly part of the future vision for electricity networks.

Many potential users of storage seem to have limited patience when they develop projects. They expect a storage solution to be possible, deliverable and achievable within weeks. The industry could respond, and we could do this, but progress has been slow that we have become used to being negative about energy storage project development.

But this marks a change in the market for storage. No longer is it the manufacturers who are pestering network companies and power companies to install electricity storage.

It is now the renewable energy developers who cannot get a connection to the network. It is the electricity distribution companies who need to control voltage. It is the consumers who do not understand why they cannot use the electricity they have just generated who are pestering manufacturers to come up with products now that meet their needs.

We have some really disruptive technologies, and we have disruptive commercial ideas. Let's just be a bit more positive that our work pestering governments, regulatory departments, power companies, network operators, consumers and everyone else who uses electricity will be rewarded with some real progress in electricity storage.

When you suffer from too much pestering, eventually the job gets done. Pester power needs to be used, not stored. \bigcirc

Anthony Price is Director of the Electricity Storage Network, the group that promotes network connected electricity storage in the UK. He is also Director of Swanbarton, a consultancy specialising in electrical energy storage. He has been active in the storage industry for 23 years and the editor of BEST magazine has been pestering him for a thought piece for only two months.



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Fuel Cells 2014 Science & Technology A Grove Fuel Cell Event



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Info:

https://powersources.net/ florida/frameset.html

24 – 26 March

Advanced Battery Power and Battery Day 2014

Muenster, Germany

Three days of expert presentations on the latest developments in lithiumion technology for EVs and stationary applications. The focus will be on the optimisation of performance, life and safety. The conference is twinned with Battery Day NRW— a platform to meet and exchange with delegates from different research fields related to energy provision, automobility and materials science. **Info:**

http://www.battery-power.eu/

25 - 27 March

Energy Storage Europe Messe Düsseldorf,

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Energy Storage 2014 focuses on storage systems and energy storage solutions in relation to the development of the energy industry in Europe. More than 800 participants will discuss the political frameworks, including the cost effectiveness of energy storage as well as innovative new financing mechanisms.

www.worldenergystorage.com

26 – 28 March 2014

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Shenzhen, China

The event focuses on lithium batteries for the EV market. Global lithium experts, leading producers and raw material manufacturers will speak about the developments in lithium battery trends, design, materials, equipment, electric vehicle technology and industry standards. **Info:**

www.ourpolaris.com/lb/index. asp

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Amsterdam, The Netherlands

A two-day event on fuel cells that would be of interest to anyone involved, or interested in, the key research and development issues facing fuel cell science and technology. including end-users. Topics of presentations include fuel cell electrochemistry, materials for fuel cells, cell and stack technology, fuels and fuel infrastructure, fuel cell systems and applications, fuel processing, modeling and control, fuel cell components. Info:

www.fuelcelladvances.com/ index.html

27 – 30 April

BCI 2014 San Diego, California, US

Battery Council International presents its 126th Convention and PowerMart Trade Fair— a convention to learn about the latest technologies, environmental issues and the impact of global economy on the battery. The PowerMart fair opening hours have been extended by two hours, to 11AM to 4PM, to give exhibitors and visitors more time to meet.

www.batterycouncil.org

26 – 28 March

Interbat Moscow, Russia

The 23rd International Specialised Exhibition "Independent Power Sources" is hosted by Russian battery association InterBat and RusBat, the national association of battery producers. This well attended event serves the growing market for energy storage in Russia and the former Soviet states. It is the ideal place to meet companies and customers from across this region in one place. The show is well attended by Asian and European lead-acid and lithiumion companies alike. Info:

http://interbat.ru/exib-e.htm

London, UK A gathering of international utility companies, transmission and distribution operators featuring speakers, including NGOs, regulators, government officials, and experts in the

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field. Discussions on the energy storage market include the points of view of utilities, generation companies, transmission & distribution challenges, renewable energy integration, wind, PV & solar issues as well as implementation of storage costs and case studies.

www.energystorageforum.com

mar14-jun14 133

5 – 7 May

Battcon 2014 Florida. USA

Battcon International Stationary Battery Conference features a non-commercial conference that will include all chemistries and applications. Alongside the conference is a two-day trade fair, and of course, golf sessions. Featuring leading stationary battery experts, the conference presents papers by users and manufacturers that relate to everyday battery applications, technical advances and the diverse concerns of the battery industry. This will incorporate manufacturing, maintenance trends, testing issues and safetv. Info:



Kyoto, Japan

The first Asian AABC brings the conference and exhibition closer to the carmakers and suppliers of the xEV market and battery technology innovators. Top energy storage technologists from Asian carmakers and their suppliers will assess the Asian electrified vehicles market and the battery technology that will power it.

http://advancedautobat.com/ conferences/

9 – 12 June

46th Power Sources Conference Orlando, Florida, USA

The Power Sources Conference looks at large-scale energy storage technology, focusing mainly on the electrochemical field. The technical conference will be accompanied by a poster session and exhibition. Conference topics will include devices, materials, mechanisms and power management, prototype development, manufacturing technology, device and system engineering, and economic and environmental considerations. Info

www.powersourcesconference.

10 – 13 June

LABAT 2014 Albena, Bulgaria

Technical conference and exhibition with open discussions in each of the conference sessions set at a beautiful Bulgarian beach resort. Topics include advanced lead-acid battery design and cell technology; electrolyte and paste additives; materials for advanced batteries and lead-carbon electrodes; supercapacitor systems; industrial machines and battery production equipment; the electrification of vehicles; and recycling. Info:

www.labatscience.com

8 – 9 May

www.battcon.com

Australian Energy Storage Conference & Exhibition

Melbourne, Australia

Australia's first on- and off-grid energy storage event is being held in Melbourne and will feature a two-day exhibition and conference showcasing technological advances, market trends and financial analysis of the energy storage market in Australia. Co-hosted with Solar 2014, this event provides an opportunity to network with companies in the Australian solar and energy storage market.

Info:

www.australianenergystorage. com.au

4-6 June Electricity Storage Association Annual Conference

Washington DC, USA

The Electricity Storage Association (ESA) is hosting its annual conference in Washington DC featuring speakers from industry and governmental departments as well as major manufacturers from the energy storage industry.

Info:

www.electricitystorage.org/ about/welcome



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DEADLINES TO REMEMBER:

Pre-registration, Short Abstract submission and reservation of exhibition space 30.10.2013

Early bird registration and submission of Extended Abstracts

15.03.2014



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Mrs. Mariana Gerganska Secretary of LABAT'2014 gerganska@labatscience.com

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ADVANCE NOTICE

14th European Lead Battery Conference and Exhibition

Edinburgh | Scotland | September 2014

The International Lead Association is pleased to announce that the 14th European Lead Battery Conference (14ELBC) and Exhibition will be held at the Edinburgh International Conference Centre, Scotland on 9-12 September 2014.

14ELBC will provide an ideal opportunity for anybody involved with the global lead battery industry to review and discuss the most recent technical advances associated with lead-acid batteries, especially in the areas of emerging new automotive and renewable energy systems.

Technical presentations at the Conference will bring delegates right up-to-date with the latest research and development information from around the globe, and will be of keen interest to both manufacturers and users of lead-acid batteries, as well as to the scientific community. An extensive Exhibition – expected to involve over 100 exhibitors - by suppliers to the industry of equipment, materials and technology, will also take place.

Since the first meeting in Paris in 1988, the European Lead Battery Conferences have developed a reputation for high quality presentations on the design, manufacture, performance and use of lead-acid batteries. Over 600 delegates and 100 exhibitors attended 13ELBC in Paris in 2012, and similar numbers are confidently expected in Edinburgh.

14ELBC Conference Secretariat:

Maura McDermott International Lead Association, Bravington House, 2 Bravingtons Walk, London N1 9AF United Kingdom Tel: +44 (0) 20 7833 8090 Fax : +44 (0) 20 7833 1611 E-mail: 14elbc@ila-lead.org





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The scope of the conference will include but not limited to the following communications power and energy systems topics:

Communications Power Systems

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- Renewable energy generations (Wind, PV, Hybrid)
- Islanded and grid-connected autonomous power systems
- Power systems (High and/or low voltage DC; High and/or low voltage AC) for central offices/data centers
- Power distribution architectures for communications equipment
- Wireless power transfer for handheld communications devices

Energy Storage for Communications Systems

- Architectures for energy storage
- Battery technology (lead, zinc, lithium, sodium)
- Flow battery technology
- New fuel cell technology
- Energy management techniques
- Energy modeling and simulation

Power Conversion for Communications Equipment

- Circuit topologies and control techniques for AC/DC, DC/DC and DC/AC power converters
- Utility interface inverters for energy generation and storage
- AC and DC UPS
- High efficiency and high density power supplies

Site Support Systems

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- Disaster recovery and mitigation
- Engine generator technology
- Physical and thermal design
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- Codes, standards and specifications



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DISCOVERED! The Higgs Boris particle

This quarter, your Scribe swapped his casual office clothes for overalls: it was time for a little home improvement and that always seems to involve home electrics. Writing about aspects of the electricity industry is one thing but doing the physical work is something else.

It's dirty and physically demanding, but hardly complex. You'd think the *Scribe* now makes sufficient remuneration to pay artisans to do the work but there's a certain pride in doing things yourself.

But these days the pleasure has been sucked out of it. Firstly there's the frustrating experience of buying all the materials at the DIY superstore. The *Scribe* can never find the stuff he needs and asking staff for help is like asking the time of day from folks on the dementia ward.

Wrestling with old British houses is a special kind of torture all of its own. The electrical wiring is usually run under heavy floorboards that were last nailed down by John Christie or some other English mass murderer.

When you eventually prise them up and are delighted not to have found the mummified body of an old whore, or a secret arms cache belonging to the IRA, it's time to locate the power cables themselves.

Then the fun begins. With the circuit breaker in the off position, carefully open the junction boxes of the circuit you wish to alter. And then trip all the lights you need to work by, because some clown has wired a residual current device across all the circuits and your finger has just grounded the neutral conductor.

Next, struggle with heavy 30A power cables and route them to new power outlets you've meticulously cut into the crumbly plaster and brick walls.... When all that is finished, it's time for a lie-down on the cold hard floor, exhausted from your efforts.

The *Scribe* learns, however, that all this could soon be a thing of the past. With domestic electrical energy storage, we'll all be benefitting from low voltage DC distribution in the home.

No more protection circuitry, no heavy conductors. We'll all be powering our consumer electronics direct from USB outlets and we'll all be cutting our electricity charges too, as a consequence; the days of rectification will be at an end. Watch out... Flying pig about!

According to our Canadian-born

boss of the Bank of England, the UK economic recovery is now the fastest in the world. Here at BEST magazine we don't buy that because the vast majority of our readers are outside the UK and virtually all our advertisers are non-UK based.

Our local high streets and shopping areas are reminiscent of poor dental hygiene— boarded-up shops, failed banks and what



Americans call thrift stores, as Amazon takes all.

The last major international battery meeting in the UK was years ago when the now-defunct International Power Sources Symposium upped sticks from Brighton. The renowned International Lead Organisation is chancing its arm with a meeting which may be the very last held in what could be a very dis-United Kingdom— the Scottish vote on independence from London rule is less than week after the European Lead Battery Conference in Edinburgh in September.

Every event we attend has much the same conference format and the inevitably ends up with a conference dinner and, my, they can be very dull affairs.

So the *Scribe* gives maximum brownie points for a small UK firm in the standby power market, which, in our humble opinion, stands head and shoulders above the so-called professional events— because he actually enjoyed the event!

It is called NIBS. Who, you ask? Northern Industrial Battery Supply— a small UK firm that takes care of everything in the critical power field— gensets, UPS and a whole lot more. NIBS went the extra mile to organise a small technical meeting to educate customers and suppliers alike on the whys and wherefores of batteries— a sort of miniature Battcon with a touch of Intelec thrown in for good measure. Someone has to. Techies need training.

From the way the UK electricity supply industry is going, NIBS could be very busy people indeed as it waits for the inevitable blackouts that are expected in coming months as demand

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exceed supply, thanks to 30 years of mismanagement by the UK Government.

The NIBS meeting was a two-day event, so an event dinner was a must. And to make to the time pass, what better than to organise a quiz as part of the dinner. And the organiser went a stage further. What better a way for bunch of hairy-arsed engineers to while away their time than problem solving?

Each table group at the dinner had to build a bridge from the contents of a packet of materials in a fixed time and then drive a small electric car over the bridge. We're talking a distance of less than two feet.

It was very animated few minutes on every table. For those of you who saw the movie Apollo 13, it will make perfect sense. Leadership and team involvement came into play, not to mention skills with Sellotape and paper rolling.

Of course, the *Scribe's* table won—little to do with the *Scribe* however. The overall effect was electric— the meeting's mood was elevated to the state of winning a European soccer tournament.

Well done Grant Brackley, commercial director at NIBS. You've shown the battery conference industry how do business, gain knowledge and have fun. Other show organisers take note — your delegates are BORED!!!!!





The 'Higgs Boris particle'

2013 was a great year for particle physics with the confirmation of the existence of the Higgs boson— the mysterious particle which gives all other particles mass. Predicted as long ago as 1964, 'proof' came by way of an experiment at the Large Hadron Collider.

In the world of electrochemistry and batteries, another

> new particle has been discovered by BEST magazine we've given it the title of the 'Higgs Boris'. The Higgs Boris operates in an extension to the standard model of the

forces and particles in the universe— twelve basic particles, electromagnetic forces, gravity and weak and strong forces: now there are three more forcescredibility, funding and cost.

The Higgs Boris can usually be observed at battery meetings and appears to be important in giving lead-acid papers extra credibility. If the Higgs Boris is not present, the attributes of lead-acid batteries can sometimes be lost and importance of the cost force, which is a constant, is not registered.

In some circumstances the Higgs Boris can reduce the funding force in other electrochemical couples to the benefit of lead-acid.

The 'take-home message', which can be found in your conference bag along with the USB drive which doesn't contain the papers you want to read— is thus: If the Higgs Boris is not present, it may be futile to deliver a presentation on lead-acid technology. However, the conditions may be perfect for delivering something like lithium FantastiCON[™].

In the next issue, the *Scribe* will investigate the role of the consultant force field. \bigcirc

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