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## Poster abstracts

### P1

#### Synthesis of $\text{Na}_x\text{V}_2\text{O}_5$ bronzes based on electrolytic $\text{V}_2\text{O}_5$ for use as the cathodes of lithium accumulators

E.M. Shembel\*, R. Apostolova, V. Nagirny

*Ukrainian State Chemical Technology University, 320005 Dniepropetrovsk, Ukraine*

D. Aurbach, B. Markovsky

*Bar-Ilan University, 52900 Ramat-Gan, Israel*

Miniaturization of electrochemical power sources for microelectronics requires us to use the technologies of thin films. Particularly, a rather simple method of an electrolytic metal oxide deposition enables the preparation of cathodes with a given thickness, beginning from a monolayer. Electrolysis allows us to design chemical composition, water content, size of crystallites, specific surface of the active mass deposited and, correspondingly, the electrochemical characteristics of the deposited products [1].

By anodic oxidation of vanadyl sulfate electrolytes, thin-layer deposits of electrolytic ( $e^-$ )  $\text{V}_2\text{O}_5$  oxides [2] and  $\beta$ -bronze  $\text{Na}_x\text{V}_2\text{O}_5$  [3] were previously obtained as cathodes of lithium accumulators. The physico-chemical, structural and electrochemical properties of  $e^-$ - $\text{V}_2\text{O}_5$  are similar to those of  $\text{V}_2\text{O}_5$  gels. It is known that by using the ion exchange properties and other characteristics of  $\text{V}_2\text{O}_5$  gel layers, one can produce films of heterogeneous oxide compounds namely,  $\text{Me}_x\text{V}_2\text{O}_5$  ( $\text{Me} = \text{Al}, \text{Fe}, \text{Na},$  and others) [4]. We have synthesized a number of vanadium oxide bronzes  $i\text{-Me}_x\text{V}_2\text{O}_5$  ( $x = \text{Na}, \text{Ag}, \text{Cu}$ ) by ion-exchange (i) methods using  $e^-$ - $\text{V}_2\text{O}_5$  as the precursor.

Descriptions of the synthesis of  $\beta$ -bronze  $i\text{-Na}_x\text{V}_2\text{O}_5$  and its investigation as a cathode material for lithium accumulators are presented. For the synthesis of  $i\text{-Na}_x\text{V}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$  was deposited as a thin layer on conducting substrates or used as a dispersed powder by the method described in reference [5]. Then, the  $e^-$ - $\text{V}_2\text{O}_5$  samples produced, were kept in contact with a solution of  $\text{VOSO}_4$  (0.2 M), containing  $\text{Na}^+$  ions ( $10\text{--}20 \text{ g l}^{-1}$ ), at  $\text{pH} = 1.8$  without passage of a current. The electrochemical characteristics of the washed and dried samples after exposure at  $20^\circ\text{C}$ , do not differ too much from those of regular  $e^-$ - $\text{V}_2\text{O}_5$ . The data from IR

spectroscopy, X-ray and thermal analysis as well as from electrochemical investigation indicate that by annealing at  $500^\circ\text{C}$  for 7 h, the  $e^-$ - $\text{V}_2\text{O}_5$  samples exposed to the  $\text{Na}^+$ -containing solutions, are transformed into the monoclinic bronze  $i\text{-Na}_x\text{V}_2\text{O}_5$ .  $i\text{-Na}_x\text{V}_2\text{O}_5$  bronze is identical to  $\beta$ -bronze which is a single phase in the range  $x = 0.22\text{--}0.40$ .

Cathodes made of  $\text{Na}_x\text{V}_2\text{O}_5$  bronze can be cycled efficiently within the range 3.70–2.40 V in commonly used electrolyte solutions such as PC, DME/1 M  $\text{LiClO}_4$  solution, yielding 150–180 Ah  $\text{kg}^{-1}$  at practical discharge currents such as  $100 \mu\text{A cm}^{-2}$ .

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\* Corresponding author

E-mail address: shembel@onil.dp.ua (E.M. Shembel)

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### P2

#### A new cathode system for lithium-ion batteries

A.G. Ritchie\*, C.O. Giwa, P. Bowles, J.C. Lee

*Defence Evaluation Research Agency, Haslar, PO12 2A0, UK*

A. Gilmour

*Lexcel Technology Ltd., Henley-on-Thames1 R69 ILU, UK*

A.C.C. Tseung, J. Silver, D. Lapharri

*The University of Greenwich, Woolwich Campus, London SE18 6PF, UK*

A new cathode system for lithium-ion batteries was announced at the 1997 International Power Sources Symposium at Brighton [1]. It uses a mixture of lithium sulphite and a transition metal oxide [2]. This system has now been studied further, both in cycling studies at DERA and Lexcel and in electrochemical studies by cyclic voltammetry at the University of Greenwich.

Cycling studies have been carried out on lithium sulphite alone and also on lithium sulphite/transition metal oxide mixtures. The initial studies on this system [1] used a pressed pellet construction for the cathode. Further studies at DERA using this construction confirmed the cycling capability of this system. Cathode coatings using the doctor blade technique are in progress and are reported in the poster.

Electrochemical studies using cyclic voltammetry at the University of Greenwich showed that lithium sulphite would cycle on its own but that higher voltages were obtained when a metal oxide was present.

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\* Corresponding author. Tel.: +44-2392-335429;  
fax: +44-2392-335102  
E-mail address: agritchie@dera.gov.uk (A.G. Ritchie)

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## P3

### Safety studies on lithium batteries using the accelerating rate calorimeter

Stelios Mores\*, Martyn Ottaway

*Thermal Hazard Technology, 1 North House, Bond Avenue, Bletchley MK1 1SW, UK*

A number of Accelerating Rate Calorimeter studies have been conducted on lithium chemistry based batteries. Temperature, pressure and self-heat rate data have been recorded as a function of time within an adiabatic environment. Focusing on the more common chemistries, a few examples are considered, taken under conditions such as shock discharge and thermal decomposition at elevated temperatures. Use is made of the data as a means of quantifying associated thermal stability hazards in storage and handling scenarios.

\* Corresponding author  
E-mail address: stelios.mores@science.org.uk (S. Mores)

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## P4

### A thermal battery using the Na/NiCl<sub>2</sub> couple

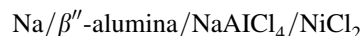
J.-Y. Poinso\*, A. Dubois, C. Barthet

*DMAT/SR2C, CEA Le Ripault, BP 16, 37260 Monts, France*

The sodium–nickel chloride cell couple is a very promising battery system, using  $\beta''$ -alumina as a solid electrolyte. The high cell voltage (2.58 V at 300°C), high theoretical specific energy (790 Wh kg<sup>-1</sup>), good cycling characteristics have made this system a good candidate for electric vehicle applications.

However, these features, the wide operating temperature range (250–570°C), and the lack of self-discharge even at elevated temperature, make this system attractive for use as a thermal battery, especially for long lifetimes and medium power applications.

The cell diagram of the sodium-nickel chloride cell couple is:



In the usual configuration, a  $\beta''$ -alumina tube separates the molten sodium (anode) and the molten sodium tetrachloroaluminate (secondary electrolyte). For thermal batteries, a bipolar configuration is required, and the first difficulties were technological obstacles.

We have begun to show that flat disc electrolyte membranes (thickness typically 0.9 mm) are thermally shock-proof even during the very rapid burning of the iron–potassium perchlorate heat pellets used to raise the temperature of thermal batteries.

We have made monopolar cells. Because sodium is liquid at the working temperature, we have used a mixture of carbon and sodium as the anode. The components for the cathode (NiCl<sub>2</sub>, NaAlCl<sub>4</sub>, C) are mixed and pressed to obtain a pellet. Carbon is used because it has a low weight and good conductive properties. The binding of the constituents is rather good, and a formation pressure of about 0.3 kg/cm<sup>2</sup> is used.

In this way, we made piles of up to five cells. The results are rather good at elevated temperatures (500–550°C). For a single cell with a diameter of 35 mm, the total resistance is about 0.1  $\Omega$  at 0.2  $\Omega$  and this does not depend on current. However, the results deteriorate when the temperature decreases (> 1  $\Omega$  at 350°C).  $\beta''$ -alumina as an electrolyte is not so good as we expected, but the resistances of the electrode–electrolyte interfaces contribute a very significant part of the overall resistance.

We are now trying to improve the performances of this system, especially by decreasing the percentage of the inactive materials — carbon, NaAlCl<sub>4</sub> — and by reducing the thickness of the electrolyte.

\* Corresponding author  
E-mail address: poinso@wanadoo.fr (J.-Y. Poinso)

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**P5****Green thermal batteries**

C. Thaler\*, S. Schoeffert

*ASB-Aerospatiale Batteries, Allée Sainte Hélène, 18021 Bourges Cedex, France*

J. Sweeney

*MSB-Missiles and Space Batteries Ltd., East Shawhead, Coatbridge ML5 4UZ, Scotland, UK*

Thermal batteries have historically been dependent on the use of chromates as the oxidising agent in either their main heat source or in the fusetrain take-over heat source from the igniter to the main chromate-free heat source. Chromates are also present in the special cells used by ASB and MSB in thermal batteries that have to meet very fast activation time requirements. This calcium anode cell technology has potassium dichromate as the depolariser. Thermal batteries using these cells can be specified to have activation times of <100 milliseconds.

Because of the health concerns associated with the use of chromates, ASB and MSB have initiated a programme to remove chromates from all their battery designs.

Our poster will present both the work that has been carried out to develop a “green” battery for a specific fast activating application and the test results obtained. The new design comprises a fast activating starter section, an existing qualified Li/FeS<sub>2</sub> power section, and a new heat paper that has been formulated without chromates but has equivalent performance to the standard material. Because the design is based on well-established manufacturing processes, it offers a low risk solution for very fast activation specification requirements.

\*Corresponding author

*E-mail address:* c.thaler@asb-group.com (C. Thaler)

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**P6****Electrode materials for power super-capacitors**

K. Jurewicz

*Institute of Chemistry and Electrochemistry, Poznan University of Technology, ul. Piotrowo 3, 60-963 Poznan, Poland*

Theoretically, very high peak power and extremely long cycle lives are the main attributes of supercapacitors as compared to electrochemical accumulators. Their

practical realisation needs the use of appropriate electrode materials.

Usefulness of the various materials can be determined from their galvanostatic, voltametric and impedance spectroscopy characteristics.

In the work presented, these techniques were used to examine carbon fibres obtained from various precursors, i.e. poly acrylonitrile, cellulose and phenol resin, also as carbon/carbon composite and carbon/conductive polymer with polyaniline or polypyrrole.

Miscellaneous conditions for pyrolysis and activation processes for obtaining of active carbon fibres were used.

The electrochemical investigations were carried out in aqueous KOH or H<sub>2</sub>SO<sub>4</sub> electrolytes. The results obtained were correlated with the electrolytic medium, the porous structure and chemical composition of the carbon materials and composites examined.

*E-mail address:* jurewicz@fct.put.poznan.pl (K. Jurewicz)

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**P7****Survey of valve-regulated lead-acid battery reliability: information exchange**

Jennifer Dunleavy

*Energetics, Inc., 501 School St. SW, Suite 500, Washington, DC 20024, USA*

Paul Butler\*

*Sandia National Laboratories, MS0613, P.O. Box 5800, Albuquerque, NM 87185-0613 USA*

Results of an investigation on the reliability of valve-regulated lead-acid (VRLA) batteries will be presented. Surveys of VRLA end-users and manufacturers have provided detailed design, operation, and field failure information for tens of thousands of installations. These data will be presented and possible interpretations of the results will be discussed. The key areas of interest have been to characterize the relationships between VRLA technologies, service conditions, performance, and field failures. Preliminary correlations will be proposed for discussion, as will estimates of VRLA battery reliability. The ultimate goal of the study will be to suggest approaches to improving field performance and life.

\*Corresponding author. Tel.: +1-505-844-7874

*E-mail address:* pbutle@sandia.gov (P. Butler)

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**P8****Advanced cellulosic membranes for silver–zinc rechargeable cells**

Harlan Lewis\*, Patricia Jackson

*NAVSEA Crane, 300 Highway 361, Crane, IN 47522, USA*

Colin Marshall

*UCB Films plc, Wigton, Cumbria CA7 9BG, England, UK*

UCB Films plc membrane materials are under evaluation as separation in model silver-zinc rechargeable cells. The cells are on a cycle life study at 100% depth-of-discharge where individual electrode voltage measurements are recorded every fifth cycle to monitor development of cell impedance and zinc shape change. Cells are withdrawn periodically for dissection to allow determination of rate of silver migration, of anode shedding and changes in membrane physical properties.

This poster will report the results of the cycle life study for both reinforced and unreinforced sausage casing with respect to the parameters under evaluation, with recommendations for their utilization in cells using rechargeable alkaline chemistry.

\* Corresponding author

*E-mail address:* lewis\_h@crane.navy.mil (H. Lewis)

PII: S0378-7753(01)00572-9

**P9****Advanced cellulosic sausage casing membranes for silver–zinc rechargeable cells**

Patricia Jackson, Harlan Lewis\*

*NAVSEA Crane, 300 Highway 361, Crane, IN 47522, USA*

Thomas Danko

*Viskase Corporation 6855W, 65th Street, Chicago, IL 60638, USA*

Viskase Corporation sausage casing membrane materials are under evaluation as separation, in conjunction with polyvinyl alcohol film, in model silver-zinc rechargeable cells. The cells are in a cycle life study at 100% depth-of-discharge where individual electrode voltage measurements are recorded every fifth cycle to monitor the development of cell impedance and zinc shape change. Cells are withdrawn

periodically for dissection to allow determination of the rate of silver migration, of anode shedding, and changes in membrane physical properties.

This poster reports the results of the cycle life study for both reinforced and unreinforced sausage casing with respect to the parameters under evaluation, with recommendations for their utilization in alkaline chemistry cells using rechargeable alkaline chemistry.

\* Corresponding author

*E-mail address:* lewis\_h@crane.navy.mil (H. Lewis)

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**P10****Perspectives on an ecological means of individual and public city transport by electric vehicles**

Miroslav Cenek

*Institute of Electrotechnology, Electrical Engineering and Computer Science, Technical University, 602 00 Brno, Czech Republic*

At the present time the application of electric vehicles both in individual and in public city transport is being developed, for ecological reasons.

First came the development of four-wheeled ecologically friendly vehicles for personal and pick-up uses. However, their application is significantly limited to use for business purposes in State administration and municipal enterprises, in spite of proven ecological benefits. Insufficient legislative support by State authorities is hindering any major expansion of this sort of city transport. Such support could eliminate the present significantly higher cost of electric vehicles when compared with vehicles using internal combustion engines (12 Euros per km after covering 120 000 km [1]).

A more significant improvement can be expected from two-wheeled electric vehicles, both for city and out-of-city operation. This concerns electric bicycles with auxiliary electric drive, folding electric scooters with two or three wheels and electric scooters of classical design.

During the last few years there has been significant development of electrobuses, ecologically friendly electric vehicles that can be purely electric or with hybrid drives. This fact is proven by the positive experiences obtained from an eight-year operation of electrobuses for city transportation in Santa Barbara, California, U.S.A. Problems associated with electrobuses with hybrid drives are being addressed by a European Union project in which the following cities are participating: Stavanger, Brugge, Luxembourg, Sintra, Alicante, Athens, Trento, Savona and Besançon.

There is a 32-year history of two and four-wheeled electric vehicles in the Czech Republic. During the eight

years since 1992, there has been intense activity both in University research, and by financial support from State Ministries in the production of electric vehicles, chargers (particularly fast-chargers) and monitoring devices for accumulators. Legislative support has started in some cities.

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E-mail address: cenek@uete.fee.vutbr.cz (M. Cenek)

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## P11

### Microporous carbons for supercapacitors<sup>☆</sup>

K. Jurewicz\*, E. Frackowiak

*Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, ul. Piotrowo 3, 60-965 Poznan, Poland*

F. Beguin

*CRMD-CNRS University, 1B rue de la Férollerie, 45071 Orléans, France*

Due to the availability of various precursors and technologically well-developed methods of modification, materials based on carbon are especially adapted for application in electrochemical capacitors. They can be used with aqueous solutions (basic and acidic) as well as in aprotic media. During the preparation of carbon material it is possible, over a wide range, to affect the microtexture and chemical composition through the selection of precursor, conditions of carbonisation and the activation process.

The method used to prepare the carbon determines the electrochemical parameters of a capacitor. Generally, the most convenient is to use carbon materials in the fibrous form, however in our case the powdered carbon obtained from petroleum coke and then chemically activated supplied high capacitance values of over 200 F g<sup>-1</sup>. Specific surface area of this carbon, as measured by nitrogen gas adsorption at 77 K, was approximately 2800 m<sup>2</sup> g<sup>-1</sup>.

Electrochemical parameters of the investigated material, which was in the form of a pellet comprising 85% of C, 10% of PVDF and 5% of AB, were determined in the two electrode 'swagelok' cell as described elsewhere

[Frackowiak et al., Appl. Phys. Lett. 77 (2000) 2421–2423] using 6 M KOH and 1 M H<sub>2</sub>SO<sub>4</sub> electrolytes. Specific capacitance was calculated from voltammetry characteristics at scan rates from 1 to 10 mV s<sup>-1</sup>, galvanostatic cycling with current densities from 50 to 1000 mA g<sup>-1</sup> and impedance spectroscopy in the range from 1 mHz to 100 kHz. Electrochemical investigations were carried out using a multichannel potentiostat/galvanostat (VMP Biologic, France) and a Solartron SI 1260. All the techniques gave comparable results of specific capacitance of carbon (approximately 270 F g<sup>-1</sup> in alkaline solution and approximately 230 F g<sup>-1</sup> in acidic medium).

The results obtained show that alkaline electrolyte is preferable for this type of carbon when used as capacitor material. During voltammetry experiments from 0 to 0.8 V, the shape of the characteristics remains perfectly rectangular even at the fast scan rates (10 mV s<sup>-1</sup>). Only in the wider range of potential (from 0 to 1.0 V) does the shape of voltammograms change slightly, but the stored charge remains the same and galvanostatic characteristics are still linear. This means that carbon material allows quick charge propagation. This is also confirmed by impedance spectroscopy (material supplies a high capacitance of over 120 F g<sup>-1</sup> at 1 Hz). This is a proof that the carbon material, apart from having a well-developed surface area, possesses the required porosity from the presence of mesopores. In acidic solution, the capacitance values are lower by about 20%, however the frequency response is better. Further investigations are planned to correlate microtexture, pore size, distribution of pores and chemical composition of carbon with capacitance parameters for aqueous as well as aprotic electrolyte solutions.

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\*Corresponding author

E-mail address: jurewicz@fct.put.poznan.pl (K. Jurewicz)

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## P12

### Lead film electrodes as both negative and positive plates of a lead-acid battery

L.A. Yolshina\*, V.Ya. Kudyakov

*Institute of High-Temperature Electrochemistry, Urals Branch of the Russian Academy of Sciences, Ekaterinburg, Russia*

As has been shown previously, the electrochemical characteristics of lead film electrodes may be significantly influenced by the materials and shape of metallic substrates. Lead layers were deposited by the currentless, contact-exchange method from a molten salt electrolyte onto pure and technical grade smooth aluminium plates and grids 300–700 μm thick and onto copper grids 100–150 μm thick.