

During the relaxation period, because no current is flowing, only diffusion processes will be occurring. The internal resistance of a cell or battery was defined as:  $R_{int,i} = (V_o - V_d)_i / I_i$  and the power from the internal resistance as:  $P_{int,i} = (V_o - V_d)_i \times I_i$  where  $I_i = V_{d,i} / R$  or  $I = \text{constant}$  and  $I = 1 \dots n$ ,  $V_{o,o} > V_{d,i} > V_{d,n} \geq V_{o,o} / 2$ .

Directly and integration by parts of internal energy losses lead to the differential equation:  $dt/t = b \cdot dP_{int} / P_{int}$ , that is, time against power relationship.

Thermodynamically, the calculation was: (1)  $V_{o,i} = (V_d + P_{int} / V_d)_i$ , where  $P_{int,i} = (t_i / a_i)^{1/b_i}$ . Using experimentally observed kinetics and the known discharge curve: ( $V_{d,i}$  versus  $t_i$ , where  $i = 1 \dots n$ ) and (2),  $dP_{int} = d\{(V_o - V_d) \cdot I\}$ , a time-independent differential equation is obtained, which can be integrated as a Clairaut's one.

By short-term discharging, that is:  $V_{o,o} > V_{d,i} > V_{d,k}$ ,  $i = 1 \dots k$ ,  $k \ll n$ ,  $V_{d,n} \geq V_o / 2$  and  $\phi < t_i < t_k \ll t_n$ , and measuring  $V_{o,o}$  and  $V_{o,k}$  by using time-dependent thermodynamic calculations ( $V_{o,i}$  versus  $V_{d,i}$ ) and  $dt/t = b \cdot dP_{int} / P_{int}$  the calculated discharge curve:  $V_{d,i}$  versus  $t_i$ ,  $i = 1 \dots n$ ,  $V_o > V_{d,i} > V_{o,n} \gg V_o / 2$  was obtained. The short-time interval,  $i = 1 \dots k$ , must be divided into: (1) initial conditions:  $V_{o,o}$ ,  $V_{d,1}$ ,  $V_{d,2}$  versus  $\phi$ ,  $t_1$ ,  $t_2$ , respectively and (2) the control sub-interval:  $V_{d,3 \dots k}$  versus  $t_{3 \dots k}$  and  $V_{o,k}$  measured after a relaxation period. Measured  $V_{o,o}$  and  $V_{o,k}$  and estimated  $V_{o,1}$  values define the  $V_{o,n}$ .

The above equations were verified by experiment and published discharge data on primary and secondary cells and batteries, ranging in size from small to stationary designs as large as 1000 Ah, with voltage strings as high as 380 V.

By the calculated discharge curve, using known thermodynamic and kinetic data, a primary or secondary cell or battery may be investigated as an electrochemical system.

## P4

### New achievements in the cycle life of the silver/zinc battery

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Shape-change and dendritic growth are the main drawbacks limiting the cycle life of the silver/zinc battery. These problems can be overcome by insertion of thin high-porous nickel membranes between the electrodes of the battery. In this poster are presented experimental data on the performance of silver/zinc batteries containing these membranes and results of cycling tests. The results reveal a substantial increase of the cycle life of the silver/zinc battery without any significant effect of the membranes on its performance.

## P5

### Development of cell components for a 20 Ah, 12 V secondary zinc/air battery

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Electrically rechargeable zinc/air-batteries are being considered for both electric vehicle and portable device applications. The high theoretical ( $1150 \text{ Wh kg}^{-1}$ ) as well as practical specific energy ( $60\text{--}150 \text{ Wh kg}^{-1}$ ) are major advantages of the secondary zinc/oxygen battery. The low cost and low toxicity of the materials involved are also an important factor.

By developing a durable perovskite-catalyzed bifunctional oxygen electrode and a long-lived pasted zinc electrode, the cycle life behaviour of secondary zinc/oxygen cells has been improved considerably [1].

The tested monopolar cells consisted of one pasted zinc electrode, having a nominal capacity of 2.5 Ah and an electrode size of  $25 \text{ cm}^2$  sandwiched between two bifunctional oxygen electrodes.

In this poster we will present the scale-up of the manufacturing method for the pasted zinc electrodes as well as for the bifunctional oxygen electrodes. The electrode size was increased from  $25$  to  $150\text{--}200 \text{ cm}^2$ . Moreover, results obtained with larger zinc/oxygen batteries having a monopolar electrode arrangement will be presented. Cycle life, discharge capacity, specific power and specific energy data of the tested batteries will be shown in relation to the results obtained with single (2.5 Ah) cells.

## References

- [1] S. Müller, F. Holzer, C. Schlatter, C. Comninellis and O. Haas, *Proc. of the Rechargeable Zinc Batteries Symposium, 188th Meeting of the Electrochem. Soc., Chicago, Oct. 1995.*

## P6

### Glassy carbon capacitor stack

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To meet the peak power demands in electric or hybrid vehicles, great efforts are being made to develop high power density, high energy density capacitors, such as electrochemical double-layer capacitors (EDC). The energy storage arises from the double-layer formed at the interface between electrolyte and electrode. Low internal resistance of the capacitor is required to reach high power.

Various electrode materials have been considered and tested. At the moment the most widespread active layer used in electrochemical capacitors is activated carbon. Metal oxides and conducting polymers are further alternatives. In our research group, interest is focussed on activated glassy carbon (GC) as electrode material [1]. The surface of the bulk glassy carbon is transformed by electrochemical or chemical activation, so that a high surface area active layer results. Either aqueous ( $\text{H}_2\text{SO}_4$ ) or organic [ $(\text{CH}_3\text{CH}_2)_4\text{-NBF}_4$  in acetonitrile] electrolyte can be used.

After the first promising results on a 20 cm<sup>2</sup> unit cell (2 F, 65 mohm at 1 kHz, 1 V dc bias) the next step was to build a GC capacitor stack with four electrodes (three unit cells). The GC electrodes were 1 mm thick and 20 cm<sup>2</sup> in area. A porous polypropylene film was used as separator which was wetted with 3 M sulfuric acid. At 3 V dc bias, a capacity of 0.3 F at 0.1 Hz was measured by ac impedance spectroscopy.

We present ac impedance data of a GC capacitor stack with up to seven unit cells with bipolar plates of 0.1 mm in thickness. The frequency dependence of the active layer capacitance will be shown. A capacity of about 1 F per unit cell is expected. In order to lower the internal resistance, much attention has been paid to the separator and the end-plate contacts.

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### Reference

- [1] M.G. Sullivan, R. Kötz, O. Haas, in F.M. Delnick and M. Tomkiewicz (eds.), *Electrochemical Capacitors, Proc. Electrochem. Soc.*, 95–29, ECS Proceedings Series, Pennington, NJ (1996), p. 198.

## P7

### Improvements in lithium/CF<sub>x</sub> cells

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The Li/CF<sub>x</sub> primary cell is very attractive to many consumers because of its high specific energy, enhanced safety, and operating voltage (close to that of an Li/MnO<sub>2</sub> cell). Recently ECO has developed an improved cathode material for Li/CF<sub>x</sub> primary cells. Based on preliminary investigations of different fluorocarbons with the same degree of fluorination, we have determined that electrochemical capacity and operating voltage of CF<sub>x</sub> material does not depend on the physical properties of the precursor material at low operating current densities (less than 0.2 mA/cm<sup>-2</sup>). However, at

higher current densities, all electrochemical parameters of CF<sub>x</sub>, including voltage delay, OCV operating voltage and electrochemical capacity increase with increased surface area of the cathode material precursor.

We have demonstrated the importance of precursor surface area in tests using ‘‘AA’’- and ‘‘D’’-size Li/CF<sub>x</sub> cells with cathode material prepared from fluorinated carbonized fibres with high surface area. As part of this work we have also developed in-house technology for densification of the cathode material, ‘‘AA’’- size cells utilizing this cathode material provide discharge capacities up to 2.5 Ah and perform extremely well at low, moderate and high rates. Such improved performance combined with long shelf life, wide operating temperature range, high OCV, enhanced safety, and minimal voltage delay makes these new ECO Li/CF<sub>x</sub> cells extremely attractive power sources.

In our poster, we present data on the performance of ‘‘AA’’- and ‘‘D’’-size cells made with this improved cathode material; performance as a function of rate (up to 350 mA for ‘‘AA’’- size), of electrolyte composition and of test temperature (from –5°C up to 160°C) will be described.

Observed cell performance exceeds that of Li/CF<sub>x</sub> cells with the same internal volume manufactured by Panasonic by at least 50%.

## P8

### The stress-controlled transport of lithium through the graphite electrode under the co-existence of two staged-phases

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Lithium transport through the graphite electrode in the coexistence of two staged-phases has been investigated in 1 M LiAsF<sub>6</sub>-EC(ethylene carbonate)/DEC(diethyl carbonate) nonaqueous solution by using a potentiostatic current transient technique supplemented by a lithium charging/discharging experiment and ac-impedance spectroscopy. An attractive interaction between the intercalated lithium ion and graphite lattice is indicated from the decreased diffusivity value with increasing lithium content in the lithiated graphite electrode in the presence of single staged-phase.

This attractive interaction gives rise to the stage transformation in the electrode, which can be accounted for by the potential plateaus in charge/discharge curves. From the results of the potentiostatic current transients, it is suggested that the stage transformation in lithiated graphite electrode is accompanied by the limited transport of lithium through the electrode for which the stress generated by staged-phase boundary is responsible. The stress-controlled transport of lithium through the graphite structure was substantiated by