

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 (H_2SO_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 cm² 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 cm² 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.

Acknowledgement

Financial support by the Board of the Swiss Federal Institutes of Technology BSIT is gratefully acknowledged.

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_x cells

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The Li/CF_x 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/MnO₂ cell). Recently ECO has developed an improved cathode material for Li/CF_x 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_x material does not depend on the physical properties of the precursor material at low operating current densities (less than 0.2 mA/cm⁻²). However, at

higher current densities, all electrochemical parameters of CF_x, 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_x 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_x 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_x cells with the same internal volume manufactured by Panasonic by at least 50%.

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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 LiAsF₆-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

the occurrence of hysteresis in the potential profile during the lithium intercalation and deintercalation.

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Effect of temperature on the performance of PMAN carbon anodes in 1 M LiPF₆/EC-DMC solution

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A considerable research effort is underway to utilize carbon and graphite materials as anodes for use in rechargeable lithium-ion cells. Graphitic materials can theoretically be charged to a composition of LiC₆ or 372 mAh g⁻¹. Some disordered carbons have been reported to reversibly store over 500 mAh g⁻¹.

During the first intercalation, however, solvent-reduction processes take place which irreversibly tie up part of the Li⁺ in a passive film. The nature and composition of the film is a function of the type of solvent and supporting electrolyte used. It is desirable to minimize the extent of passive-film formation while maintaining a high reversible capacity for intercalation. To gain an understanding as to the kinetics of passive film formation, the intercalation process was examined as a function of temperature for carbons derived from a polymethacrylonitrile (PMAN)-divinylbenzene (DVB) copolymer. Both the irreversible and reversible capacities of the PMAN carbons were measured during galvanostatic cyclic experiments with 1 M LiPF₆/ethylene carbonate (EC)-dimethyl carbonate solution between 2 V and 0.01 V versus Li/Li⁺ at temperatures of 5, 21 and 35°C. Cyclic voltammetric experiments between 3 V and 0.01 V were used to obtain supplemental information. Complex impedance spectra were taken as a function of voltage during intercalation to derive kinetic information of the intercalation and passive-film processes.

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Bismuth compounds as cathodic material for lithium accumulators

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Several groups of bismuth-containing oxide compounds (BCOC) were investigated to use as cathodic materials in

lithium accumulators. Galvanostatic characteristics of composite BCOC-based electrodes have been obtained in PC, DME/1 M LiClO₄ electrolyte.

BiXO₃ (X = Eu, Sm) compounds have been assigned to the first group of BCOCs investigated.

The OCV of Li/BiXO₃ is 3.1 to 3.2 V. During cycling at a current density of 2 mA cm⁻² for six cycles, the following specific discharge capacities (Ah kg⁻¹) were obtained:

	Cycle number					
	1	2	3	4	5	6
BiEuO ₃	145	140	130	100	75	76
BiSmO ₃	320	315	200	158	140	148

At the first cycle of this BCOC group, the discharge curve is characterised by the voltage plateau of 1.7–1.4 V which increased up to 2.1–2.0 V in the subsequent cycles.

In the second group of BCOC, Aurivillius [1,2] phases, Li/Bi₄Ti₃O₁₂ and Bi₄V₂O₁₁ have been investigated. On discharge at 1 mA cm⁻² to 1.1 V, on the first cycle, bismuth titanate gave 325 Ah kg⁻¹ and 490 Wh kg⁻¹. During the next three cycles, capacity dropped to 175, 180 and 170 Ah kg⁻¹, over the voltage range 4 to 1.1 V.

Bi₄V₂O₁₁ was also investigated in monocrystalline form. The lithium/bismuth vanadate has the following characteristics: OCV = 3.1 V. Plateau voltage on first discharge at 0.1 mA cm⁻² was 1.8 V and the capacity to 1.1 V was 390 Ah kg⁻¹. Capacity decreased with cycling (Ah kg⁻¹). 2nd: 241, 3rd: 175, 4th: 108, 5th: 102, 6th: 103.

In the third group investigated, BCOC was a mixture of PbBi₂O₃ + Bi₄Ti₂O₃. The OCV was 3.1 to 3.15 V and capacity 575 Ah kg⁻¹ at 0.1 mA cm⁻² down to 1.1 V, or 260 Ah kg⁻¹ to 1.5 V.

These first results are encouraging. For practical accumulators, more investigations are necessary.

References

- [1] B. Aurivillius, *Ark. Kemi.*, (1949) 463.
- [2] B. Aurivillius, *Ark. Kemi.*, (1949) 499.

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Modelling and optimization of the parameters of the lithium/nonaqueous electrolyte interface in high energy power sources

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The problem of passivating film formation on lithium surfaces and the influence of the properties of this film is of