

K. W. Leitner · M. Winter · J. O. Besenhard

## Composite supercapacitor electrodes

Received: 15 November 2002 / Accepted: 11 June 2003 / Published online: 5 August 2003  
© Springer-Verlag 2003

In order to minimize the binder content of the supercapacitor electrodes we tried a novel concept of electrode preparation: We performed carbon precipitation on a current collector substrate by a method which has been developed in our laboratory: substrate induced coagulation (SIC) [1]. Basically, the thickness of the carbon coatings which can be prepared in one 4-step dipping cycle (1 coagulation inducer, 2 rinse, 3 carbon dispersion, 4 rinse) is in the order of a few hundred nm. The required contact time in the carbon dispersion is about 2 min, prolonged contact time does not increase the amount of deposited carbon significantly. By additional dipping cycles more carbon can be deposited. Finally, practically binder-free carbon black based supercapacitor electrodes are achieved [2]. The specific capacitance of the electrodes made by the SIC process was not as high as expected ( $C = 23 \text{ F g}^{-1}$ ). Consequently an activation step was introduced to improve the electrode porosity: Oxidation of carbon and residual polyelectrolyte was performed by dipping in nitric acid (30%) for 12 h at 40 °C. The oxidation step led to a significant increase of capacitance ( $C = 50 \text{ F g}^{-1}$ ).

Highly reversible redox active substances attached to the electrode surface as a very thin film can even enlarge the charge storage capabilities, especially when the capacity of the redox active compound (pseudo-capacitance) is available in addition to the double layer capacitance [3]. After preparation of the electrodes, two different electroactive polymers have been electrodeposited on the surface of the carbon electrode.

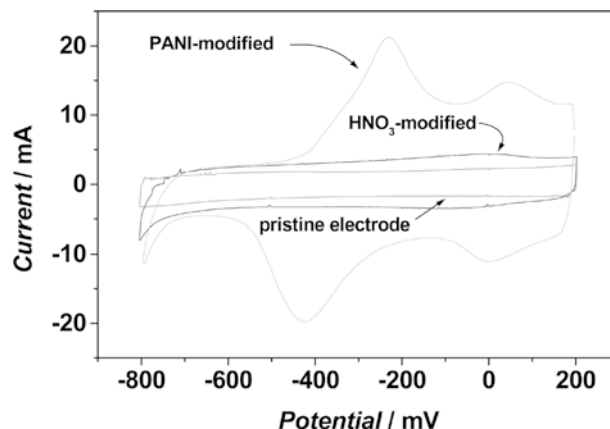
The properties of polyaniline (PANI) films has been studied extensively [4]. Due to PANI's promising application as supercapacitive material, we decided to use it as

electroactive polymer electropolymerized on our carbon electrodes (Fig. 1).

As a new category of electrochemical capacitor material, a supramolecular polymer of 1,5-diamino-antrachinone was proposed and studied in ref [5]. The polyDAAQ involves the same structure as PANI. We electropolymerized the DAAQ as well on the surface of another carbon electrodes (also made using the SIC-process) under the conditions mentioned in ref [5] and tested the electrochemical behavior (Fig. 2).

### Conclusion

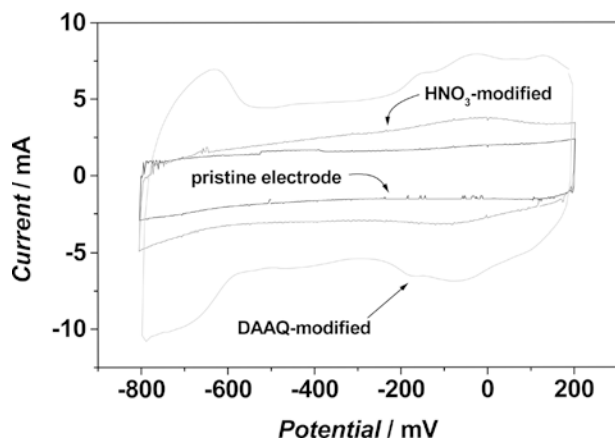
Fine particulate carbon black electrodes for supercapacitors have been prepared using the SIC-process. The specific capacitance of these electrodes were low ( $C = 23 \text{ F g}^{-1}$ ), but could be increased significantly in an oxidation step ( $C = 50 \text{ F g}^{-1}$ ). It is certain that the carbon electrodes made using the SIC process do not show any loss of active material or of flexibility when



**Fig. 1** CVs of PANI and  $\text{HNO}_3$  modified carbon black electrode, made using the SIC-process, at a potential range of  $-800 \text{ mV}$  to  $200 \text{ mV}$  vs.  $\text{Hg} / \text{Hg}_2\text{SO}_4$  in  $0.5 \text{ M H}_2\text{SO}_4$ . Scan rate =  $20 \text{ mV s}^{-1}$ . A  $10 \text{ mm} \times 10 \text{ mm}$  Ti grid was used as current collector

Presented at the 3rd International Meeting "Advanced Batteries and Accumulators", June 16th–20th 2002, Brno, Czech Republic

K. W. Leitner (✉) · M. Winter · J. O. Besenhard  
Institute for Chemical Technology of Inorganic Materials,  
TU Graz, Stremayrgasse 16, 8010 Graz, Austria  
E-mail: klaus.leitner@TUGraz.at



**Fig. 2** CVs of poly(DAAQ) and  $\text{HNO}_3$  modified carbon black electrode, made using the SIC-process, at a potential range of  $-800$  mV to  $200$  mV vs.  $\text{Hg} / \text{Hg}_2\text{SO}_4$  in  $0.5$  M  $\text{H}_2\text{SO}_4$ . Scan rate =  $20$   $\text{mV s}^{-1}$ . A  $10$  mm $\times$  $10$  mm Ti grid was used as current collector

dipping in different organic solvents. Due to this fact, carbon black supercapacitor electrodes prepared by the SIC process seem to be very suitable as substrates

for electrodeposition of electroactive polymers on the surface of these carbon electrodes. PANI as well as polyDAAQ have been electropolymerized successfully on the carbon black electrode surface. The capacitance of these carbon black electrodes could be significantly increased.

**Acknowledgement** Support by the Austrian Science Fund in the special research program "Electroactive Materials" is gratefully acknowledged.

## Reference

1. Besenhard JO, Claussen O, Gausmann H-P Meyer H, Mahlkow H (1998) US Patent 5 705 219
2. Leitner KW, Möller K-C, Winter M, Besenhard JO (2002) "Binder-free" supercap electrodes processed from high surface area fine particulate carbon black. 3rd Annual Meeting of Advanced Batteries and Accumulators, Brno, 2002 (in press)
3. Conway BE, Birss V, Wojtowicz W (1997) *J Power Sources* 66:1
4. Dinh HN, Vanýsek P, Birss VI (1997) *J Electrochem Soc* 146 (9):3324
5. Naoi K, Suematsu S, Hanada M, Takenouchi H (2002) *J Electrochem Soc* 149 (4):A472