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Chemical Capacitor Based on Activated Carbon Powder and Poly(vinyl alcohol)-H_2SO_4 Proton Conducting Polymer Electrolyte

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A totally solid state electric double layer capacitor was fabricated using a PVA-H_2SO_4-H_2O polymer electrolyte and activated carbon powder (ACP) as an electrode material. The polymer electrolyte served both as a separator as well as a binder of carbon powder. The PVA-H_2SO_4-H_2O (separator) as well as PVA-H_2SO_4-H_2O-ACP foils were prepared by the solution cast technique. The electric performance of the capacitors was investigated by cyclic voltammetry, galvanostatic charging/discharging and impedance spectroscopy. The prototype capacitors were assembled by contacting three foils (electrode + electrolyte + electrode) having a thickness of *ca.* 1.5–2 mm, a diameter of 1.8 cm and a capacity of *ca.* 0.6–1.5 F. The specific capacitance of ACP was estimated to be of *ca.* 130 F/g.

Key words: activated carbon, poly(vinyl alcohol), polymer electrolyte, supercapacitor

Chemical double layer capacitors, often called supercapacitors, consist of an electrolyte sandwiched between two blocking electrodes. The energy is stored in the electric double-layer at the electrode-electrolyte interface, therefore, capacitors are usually fabricated from activated carbons possessing specific surface area of the order of 10^3 m^2/g. Many papers have been published on various types of carbon electrodes, such as graphite (G), carbon black (CB), activated carbon powder (ACP), activated carbon fabrics (ACF) and carbon aerogel (CA). Aqueous as well as organic solutions of electrolytes have been used for the assembly of capacitors, some of them have been commercialized yet [1]. Since the electrodes are blocking, Faradaic processes are eliminated or minimized, and hence, such capacitors are characterized by a high reversibility and durability. Studies on supercapacitors using solid electrolytes have been limited till now to a number of gel-type polymer electrolytes [2–13]. Recognition of the potential application of polymer-salt complexes as solid electrolytes resulted in the development of various polymer electrolytes, including those with a protonic conduction [14–40] or alkaline electrolytes [41–45]. Proton conducting solid electrolytes may be based on a polymer matrix, which possesses ionogenic groups, such as $-SO_3H$ (polyelectrolytes); a proton exchange membrane NAFION® may serve here as an example. The second group of proton conducting membranes is

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based on complexes of strong inorganic acids, usually H_3PO_4 or H_2SO_4, with such polymers as poly(ethylene oxide), poly(vinyl alcohol) (PVA), poly(ethylene imine), poly(acrylamide), poly(methylmethacrylate), poly(benzimidazole) or poly(vinyl acetate). Replacing liquid electrolytes by solid polymer electrolytes with a conductivity of *ca.* 10^{-3} S/cm is especially useful, due to the easy handling. In a previous study, we fabricated an alkaline all-plastic capacitor, which displayed high specific capacity of the order of 90 F per gram of carbon [13]. In this work an all-plastic supercapacitor based on H_2SO_4 containing polymer electrolyte is described.

EXPERIMENTAL

Poly(vinyl alcohol) (PVA), molecular weight 100 000 (Fluka), as well as sulphuric acid (Aldrich) were used as received. Activated carbon powder was purchased in Fluka (Cat. No 231533, loss on drying ~ 10 wt. %) and in Aldrich (Darco ®, American Norit Co. Inc., Cat. No 27,809-2, specific surface of 1500 m^2/g, ~27 wt. % of humidity). The PVA-H_2SO_4-H_2O films were prepared by means of the solution cast technique. A polymer suspension in 1 mol/dm^3 H_2SO_4 was left at 60°C for 72 hours. The swollen polymer formed a homogeneous solution, which was mixed with 6 mol/m^3 H_2SO_4 solution. The resulting viscous PVA+H_2SO_4+H_2O solution was cast onto a teflon plate and weighed immediately. The water excess was evaporated slowly at ambient temperature. After evaporation, the plate with the foil, typically of a thickness between 0.2–0.5 mm, was weighed again and the composition of the electrolyte was determined from the mass balance, taking into account that water was the only volatile component of the system. Electrodes were prepared in a similar way; activated carbon powder and acetylene black (or graphite) were added to the PVA+H_2SO_4+H_2O solution and stirred thoroughly to obtain homogeneous suspension of carbon materials before casting it onto the teflon plate. The thickness of the electrodes was in the range of 0.8–1.0 mm. The composition of the electrodes was determined from the mass balance, taking into account the water content in carbon materials. Both the polymer electrolytes as well as electrodes had a form of flexible foils. Capacitors were assembled by sandwiching the PVA+H_2SO_4+H_2O electrolyte foil, playing a role of a separator, between two PVA+H_2SO_4+H_2O+AB+ACP electrodes, all having a coin-type shape (diameter of 18 mm, surface area 2.52 cm^2). Pressing across the cell lowered the thickness of the separator, and therefore the distance and ohmic resistance between both electrodes. The composition of both electrodes was identical. After assembling the capacitors, they were placed into a test vessel, and the system was left for at least 24 h at about 50°C, in order to reach the equilibrium between the electrodes and the electrolyte. Complex impedance spectra were developed by sandwiching capacitors between two platinum electrodes of the surface of 2.52 cm^2 covered with graphite (Pt|C|electrolyte|C|Pt cell), using an ATLAS 9121 frequency response analyser coupled with an ATLAS 9131 electrochemical interface (both from Atlas-Sollich, Poland). The performance of capacitors was analyzed by cyclic voltammetry (µAutolab Universal Electrochemical Analyser, EcoChemie, the Netherlands) and galvanostatic cycling (ZT-980-4 galvanostat, Unitra, Poland).

RESULTS AND DISCUSSION

Composite materials based on PVA and sulphuric acid, both with or without activated carbon powder, showed rubber-like elasticity and good moulding properties. Both types of foils (electrolyte and electrode) were somewhat sticky, and therefore, after assembling the capacitor from two electrode foils and the electrolyte foil they were brought into contact by means of pressing across the cell. This property of the system may be important in the case of fabrication capacitors of relatively high voltages. Aqueous systems imply the necessity for operating at voltages lower than approximately 1 V. Higher voltages require stacking capacitor electrodes in series. The main difficulty in constructing such a multielectrode capacitor is to ensure that all electrodes have the same capacitance C and series resistance R_S. Otherwise there is a danger of overcharging the electrode which differs, and results in the decomposition of the electrolyte. In the case of electrodes based on PVA-H_2SO_4-H_2O electrolyte, it is much easier to produce foils of identical composition and thickness even in the case of large electrodes.

Figure 1 shows an example of a cyclic voltammogram of a capacitor measured at two sweep rates: 1.5 and 5 mV/s. As may be seen from the figure, curves show a rectangular, box-like shape, typical of electrochemical capacitors. The "rounding" of the rectangular curve, which occurs following each sweep reversal, is due to the heterogeneity of the capacitor electrodes. Marked degradation of capacitive behaviour was observed when the system was tested at higher sweep rates. At sweep rates of 30 mV/s and higher, the capacitive behaviour was increasingly lost and the voltammetric curve became more and more 'ohmic' (linear). The capacity of the device, characterized in Figure 1, was 0.6 F, which corresponds (taking into account the total mass of ACP in the device) to a specific capacitance of 127 F/g of active electrode material (ACP, Norit Inc.). A value of *ca.* 120–135 F/g was obtained for different capacitors and different ACP concentration in electrodes (6–25 wt. % of ACP, Norit Inc.). The value of capacitance can be also determined from the galvanostatic charge/discharge

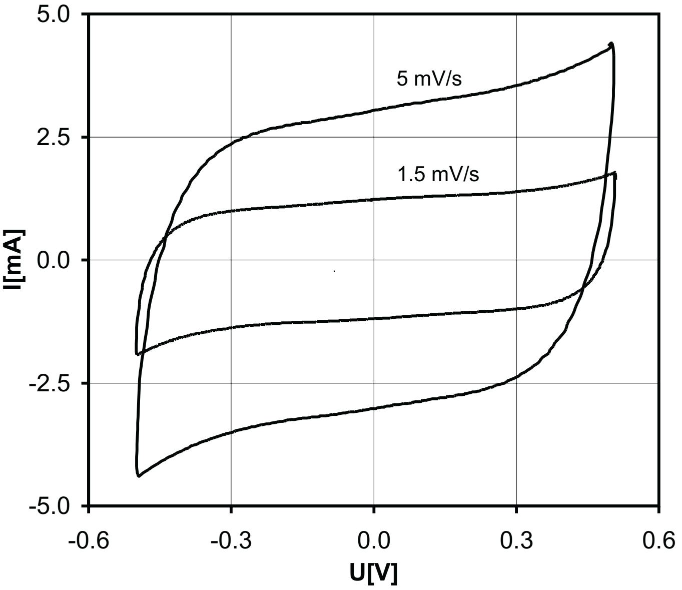

Figure 1. Cyclic voltammogram of a capacitor, consisting of two electrodes of the mass of 0.0976 g and 0.1008 g, of the composition PVA (31 wt. %), H_2SO_4 (26 wt. %), H_2O (31 wt. %), ACP (10 wt. %), acetylene black (2 wt. %); the electrolyte composition: PVA (42 wt. %), H_2SO_4 (34 wt. %), H_2O (24 wt. %). Scan rates 1.5 and 5 mV s^{-1}.

characteristics (Figure 2). The specific capacitance obtained in this way reached 130 F/g, comparable to that estimated from cyclic voltammetry. Applying of activated carbon powder supplied by Fluka led to a somewhat lower specific capacitance of approximately 110 F/g. An example of self-discharge data is presented in Figure 3. Typically, after about 300 minutes a decrease of the potential difference between both electrodes by *ca*. 50% was observed. The ageing effect is shown in Figure 4; after about 1 year the capacity decreases by *ca*. 50%. The impedance plot shown in Figure 5 consists of a small arch at high frequencies and a linear part at low frequencies. The linear part of the plot corresponds to the impedance of the capacitance, while the total impedance of the device is attributed to the semicircle in the high frequency range. For an ideal, pure capacitive element the real and imaginary components of impedance should be out of phase by 90°, independent of frequency. Chemical capacitors exhibit an equivalent series resistance R_S, due to the electrolyte resistance as well as all contact resistances, which gives rise to a phase angle that is frequency dependent. For a series RC circuit $Z(\omega) = R_S - i/\omega C$ and therefore, the $Z'' = f(Z')$ plot is a line with the high-frequency intercept being R_S. Moreover, electrodes built of particles of high-area activated carbons cannot be represented by a simple RC circuit, but rather by equivalent circuits involving distributed capacitance with ohmic elements both in series and parallel. One may also take into account pseudocapacitance, due to Faradaic processes associated with surface functionalities on the interface of carbon material. In such a case, for the series (R_S) and parallel (R_P) combination the com-

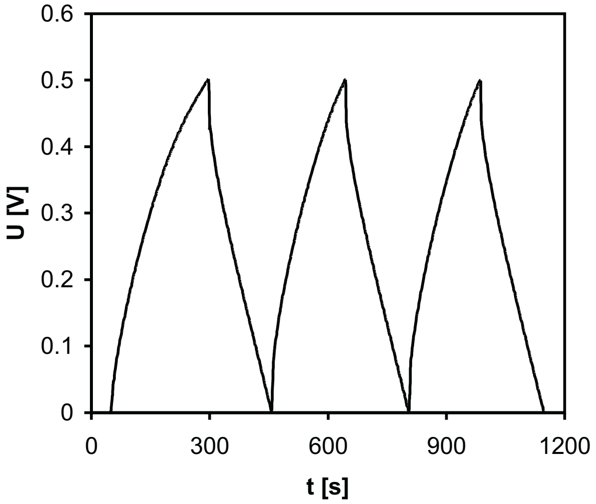

Figure 2. Galvanostatic charging of a capacitor consisting of two electrodes of the mass of 0.2568 g and 0.2288 g, of the composition PVA (24 wt. %), H_2SO_4 (42 wt. %), H_2O (16 wt. %), ACP (15 wt. %), acetylene black (3 wt. %); the electrolyte composition: PVA (41 wt. %), H_2SO_4 (48 wt. %), H_2O (11 wt. %).

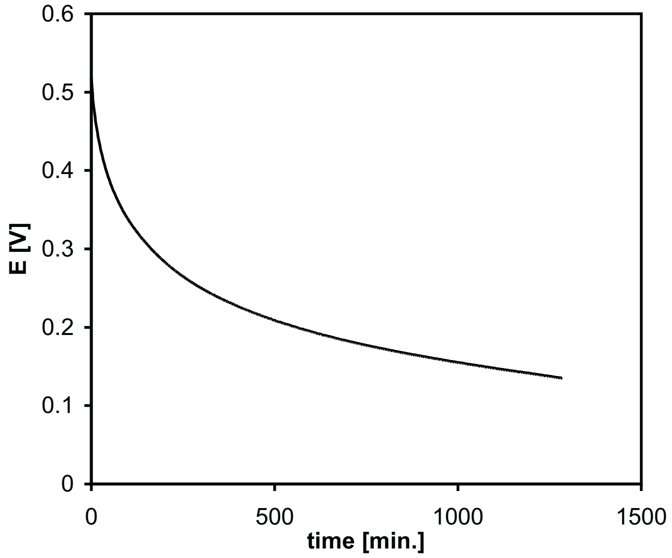

Figure 3. Self-discharge of a capacitor consisting of two electrodes of the mass of 0.2568 g and 0.2288 g, of the composition PVA (24 wt. %), H_2SO_4 (42 wt. %), H_2O (16 wt. %), ACP (15 wt. %), acetylene black (3 wt. %); the electrolyte composition: PVA (41 wt. %), H_2SO_4 (48 wt. %), H_2O (11 wt. %).

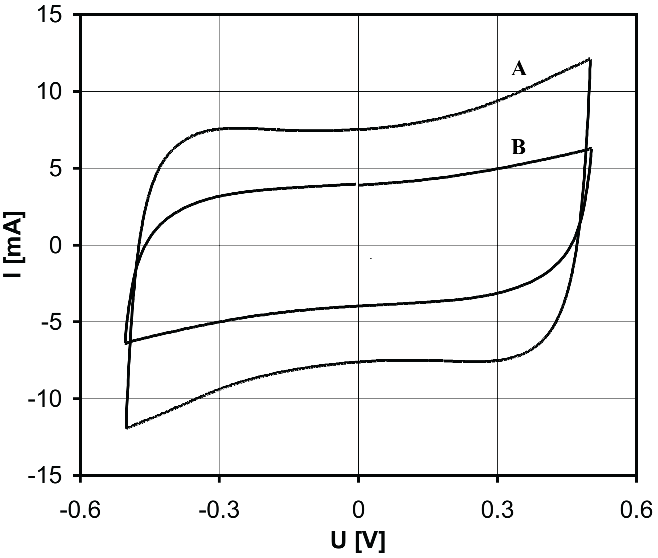

Figure 4. Cyclic voltammogram of a capacitor consisting of two electrodes of the mass of 0.2350 g and 0.2205 g, of the composition PVA (23 wt. %), H_2SO_4 (25 wt. %), H_2O (27 wt. %), ACP (16 wt. %), graphite (9 wt. %); the electrolyte composition: PVA (41 wt. %), H_2SO_4 (31 wt. %), H_2O (28 wt. %). **A**: freshly prepared, **B**: after 1 year of storage.

plex-plane plot has the form of a semicircle, which transforms at Z′ = $R_S + R_P$ to a vertical line with decreasing frequency, with an intercept at R_S on the Z′ axis as $\omega \rightarrow \infty$. On the other hand, the Z″ value at $\omega \approx 0$ corresponds to the impedance of the pure capacitor. R_S determines the rate, at which the supercapacitor can be charged/discharged and limits the power of the device. Consequently, the R_SC product corresponds to a time at which the capacitor can be charged or discharged. Therefore, the minimization of R_S is desirable in constructing supercapacitors. From the intersecting point of the semicircle with the real axis, *ca.* 0.75 Ω for the R_S can be obtained from Figure 5. Gel-type proton conducting electrolytes, including PVA-H_2SO_4-H_2O system, consist of a polymer matrix swollen with water, where acid dissociates to form H_3O^+, and the system exhibits liquid-like protonic conductivity in the solution entrapped in the polymer matrix. The conductivity of the PVA-H_3PO_4-H_2O system is *ca.* 10^{-3} S/cm at 30°C [26], while the PVA-H_2SO_4-H_2O electrolyte shows an even better conductivity: 10^{-2} S/cm [40]. Literature data indicate, that gel-type polymer electrolytes based on PVA as polymer matrix, PVA-(H_2SO_4, H_3PO_4, CF_3SO_3H or H_3PO_2)-H_2O exhibit conductivities of 10^{-3}–10^{-2} S/cm at room temperature [13,36,40,46], satisfactory for practical application in supercapacitors. The PVA-

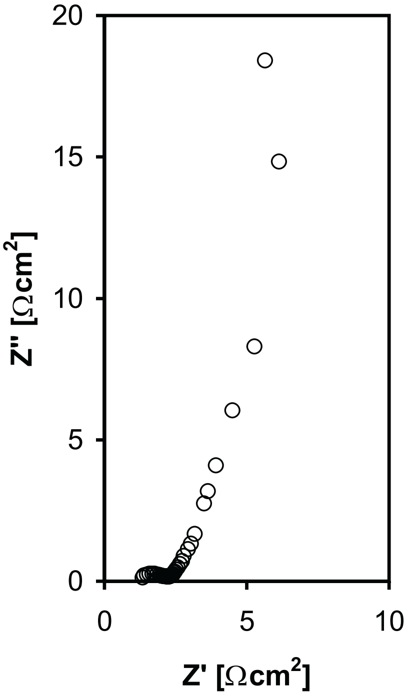

Figure 5. Impedance spectrum of a capacitor consisting of two electrodes of the mass of 0.2350 g and 0.2205 g, of the composition PVA (23 wt. %), H_2SO_4 (25 wt. %), H_2O (27 wt. %), ACP (16 wt. %), graphite (9 wt. %); the electrolyte composition: PVA (41 wt. %), H_2SO_4 (31 wt. %), H_2O (28 wt. %).

H_3PO_4 polymer electrolyte was used in the construction of supercapacitors, based on high density graphite or activated carbon fabrics with the specific surface of 2000 m^2/g [6]. The capacitors based on activated carbon fabric had large capacitance of 0.36–0.47 F/cm^2, equivalent to 70–90 F/g (of ACF). A supercapacitor based on the proton conducting electrolyte Nylon6,10-H_3PO_4 and activated carbon fabrics (2000 m^2/g, specific conductivity 10^2–10^3 S/cm) has also been developed [3]. The capacity increased between 50 F/g at –5°C to 80 F/g at 55°C, and this was attributed to the decrease of the viscosity of electrolytes, improving the micro-accessibility to smaller pores. Electric double-layer capacitors were also fabricated using PVA-containing silica gel doped with $HClO_4$ and ACP [8]; the capacity was of the order of 44 F/g (of ACP).

CONCLUSIONS

An all-plastic double layer capacitor, based on activated carbon powder, as electrodes material, and PVA-H_3PO_4-H_20 polymer electrolyte playing the role of both separator and carbon binder, can be fabricated. Specific capacity reaches *ca*. 110–130 F/g (of ACP), with low value of equivalent series resistance. As the system contains water, fabrication of the device would not demand moisture-free conditions. Moreover, all components of the system are inexpensive materials, and therefore, the capacitor would be economically reasonable.

Acknowledgments

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REFERENCES

1. Conway B.E., Electrochemical Supercapacitors, Kluwer Academic/Plenum Publishers, NY (1999).
2. Matsuda Y., Morita M., Ishikawa M. and Ihara M., *J. Electrochem. Soc.*, **140**, L109 (1993).
3. Lassegues J.-C., Grondin J., Becker T., Servant L. and Hernandez M., *Solid State Ionics*, **77**, 311 (1995).
4. Liu X. and Osaka T., *J. Electrochem. Soc.*, **143**, 3982 (1996).
5. Liu X., Momma T. and Osaka T., *Chem. Lett.*, 309 (1996).
6. Hashmi S.A., Latham R.J., Linford R.G. and Schlindwein W.S., *J. Chem. Soc. Farad. Trans.*, **93**, 4177 (1997).
7. Osaka T., Liu X. and Nojima M., *J. Power Sources*, **74**, 12 (1998).
8. Matsuda A., Honjo H., Tatsumisago M. and Minami T., *Solid State Ionics*, **113–115**, 97 (1998).
9. Matsuda A., Inoue K., Takeuchi H. and Okuhama Y., *Solid State Ionics*, **113–115**, 103 (1998).
10. Ingram M.D., Pappin A.J., Delalande F., Poupard D. and Terzulli G., *Electrochim. Acta*, **43**, 1601 (1998).
11. Matsuda A., Honjo H., Hirata K., Tatsumisago M. and Minami T., *J. Power. Sources*, **77**, 12 (1999).
12. Osaka T., Liu X., Nojima M. and Momma T., *J. Electrochem. Soc.*, **146**, 1724 (1999).
13. Lewandowski A., Zajder M., Fr¹ckowiak E. and Béguin F., *Electrochim. Acta*, **46**, 2777 (2001).
14. Donoso P., Gorecki W., Berthier C., Defendini F., Poinsignon C. and Armand M., *Solid State Ionics*, **28–30**, 969 (1988).
15. Daniel M.F., Desbat B., Cruege F., Trinquet O. and Lassegues J.C., *Solid State Ionics*, **28–30**, 637 (1988).
16. Petty-Weeks S., Zupancic J.J. and Swedo J.R., *Solid State Ionics*, **31**, 17 (1988).
17. Daniel M.F., Desbat B. and Lassegues J.C., *Solid State Ionics*, **28–30**, 632 (1988).

18. Przy³uski J. and Wieczorek W., *Synthetic Metals*, **45**, 323 (1991).
19. Przy³uski J., Wieczorek W. and G³owinkowski S., *Electrochim. Acta*, **37**, 1733 (1992).
20. Przy³uski J., D¹browska A., Styœ S. and Wieczorek W., *Solid State Ionics*, **60**, 141 (1993).
21. Rodriguez D., Jegat C., Trinquet O., Grondin J. and J. Lassègues C., *Solid State Ionics*, **61**, 195 (1993).
22. D¹browska A. and Wieczorek W., *Materials Science and Engineering*, B22, 107 (1994).
23. Wieczorek W., Florjañczyk Z. and Stevens J.R., *Electrochim. Acta*, **40**, 2327 (1995).
24. Grondin J., Rodriguez D. and Lassègues J. C., *Solid State Ionics*, **77**, 70 (1995).
25. Tanaka R., Yamamoto H., Kawamura S. and Iwase T., *Electrochim. Acta*, **40**, 2421 (1995).
26. Gupta P.N. and Singh K.P., *Solid State Ionics*, **86–88**, 319 (1996).
27. Stevens J.R., Wieczorek W., Raducha D. and Jeffrey K.R., *Solid State Ionics*, **97**, 347 (1997).
28. Vaivars G., Kleperis J., Azens A., Granqvist C.G. and Lusis A., *Solid State Ionics*, **97**, 365 (1997).
29. Przy³uski J., Po³tarzewski Z. and Wieczorek W., *Polymer*, **39**, 4343 (1997).
30. Kreur K.D., Fuchs A., Ise M., Speath M. and Maier J., *Electrochim. Acta*, **43**, 1281 (1998).
31. Fontanella J.J., Wintersgill M.C., Wainright J.S., Savinell R.F. and Litt M., *Electrochim. Acta*, **43**, 1289 (1998).
32. Bouchet R. and Siebert E., *Solid State Ionics*, **118**, 287 (1999).
33. ¯ukowska G., Rogowska M., Wêczkowska E. and Wieczorek W., *Solid State Ionics*, **19**, 289 (1999).
34. Vaivars G., Azens A. and Granqvist C.G., *Solid State Ionics*, **19**, 269 (1999).
35. Bozkurt A., Ise M., Kreuer K.D., Meyer W.H. and Wegner G., *Solid State Ionics*, **125**, 25 (1999).
36. Vargas M.A., Vargas R.A. and Mellander B.-E., *Electrochim. Acta*, **45**, 1399 (2000).
37. ¯ukowska G., Zygadlo-Monikowska E., Langwald N., Florjañczyk Z., Borkowska R., Kuzma P., Wieczorek W., Greenbaum S. and Chung S. H., *J. New Mat. Electrochem. Systems*, **3**, 51 (2000).
38. Ericson H., Svanberg C., Brodin A., Grillone A.M., Panero S., Scrosati B. and Jacobson P., *Electrochim. Acta*, **45**, 1409 (2000).
39. Honma I., Takeda Y. and Bae J.M., *Solid State Ionics*, **120**, 255 (1999).
40. Lewandowski A., Galiñski M. and Skorupska K., prepared for publication.
41. Fauvarque J.F., Guinot S., Bouzir N., Salmon E. and Penneau J.F., *Electrochim. Acta*, **40**, 2449 (1995).
42. Guinot S., Salmon E., Penneau J.F. and Fauvarque J.F., *Electrochim. Acta*, **43**, 1163 (1998).
43. Lewandowski A. and Skorupska K., *Polish J. Chem.*, **72**, 2635 (1998).
44. Vassal N., Salmon E. and Fauvarque J.-F., *Electrochim. Acta*, **45**, 1527 (2000).
45. Lewandowski A., Skorupska K. and Maliñska J., *Solid State Ionics*, **133**, 265 (2000).
46. Lewandowski A. and Skorupska K., *Polish J. Chem.*, **75**, 1745 (2001).