'Ladder-doped' polypyrrole: a possible electrode material for inclusion in electrochemical supercapacitors?

Malcolm D. Ingram [a],*, H. Staesche [b], K.S. Ryder [c]

[a] *Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, UK*
[b] *Institute of Physical Chemistry, University of Muenster, Muenster, Germany*
[c] *Department of Chemistry, Loughborough University, Loughborough LE11 3TU, UK*

Abstract

Polypyrrole (pPy) electrodes containing polysulfonated aromatic anions are investigated by cyclic voltammetry as electrodes for use in electrochemical supercapacitors. These 'ladder-doped' materials are deposited as thick films (ca. $10\,\mu m$) having open structures that permit the rapid insertion/ejection (up to $300\,mV\,s^{-1}$) of cations and anions from aqueous solution, and give an effective or 'geometric' capacitance of up to $0.40\,F\,cm^{-2}$. The 'dual mode' doping behaviour seems essential for good capacitive response. These electrodes show a remarkable tendency to perform better at high cycling rates, an effect attributed to the way the structure 'self-organises' during the self-doping process. Good electrode response depends on protecting the open structure containing hydrophilic ion-conducting channels.
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1. Introduction

Interest in the development of energy sources for electric vehicles has stimulated research into electrochemical supercapacitors, to be used in combination with fuel cells or indeed internal combustion engines to release and store energy during acceleration and braking, i.e. within approximately $10\,s$ [1–8]. The supercapacitor needs to have a high-power but not necessarily a high-energy density. The essential requirement is for *fast electrochemistry*. This can be achieved either 'non-faradaically' by double layer charging of the large internal surface of activated carbons, or by the 'double insertion' (i.e. doping) of ions and electrons into thin layers of electroactive material.

This electroactive material could be a conducting polymer such as polypyrrole (pPy). When the polymer is being oxidised anodically, it becomes p-doped and in the case of pPy, one *additional* electron can be removed for every third monomer (C_4H_3N) unit in the chain. In effect, seven electrons must be removed for every three monomer units being deposited. The residual positive charge on the polymer is balanced by the negative charge on a dopant anion. This essentially faradaic process imparts a large *capacitive re-sponse*; the electrode potential in pPy increases more or less linearly with the state of charge as would also be the case for a double layer device.

But are there any advantages in using electroactive polymers in preference to activated carbons? Early work in our laboratory [9] showed that while faster response was achievable with pPy electrodes in propylene carbonate (PC)-based electrolytes, the inherently large capacitance of such electrodes was accessible only in thin films (ca. $1\,\mu m$ thick), apparently because of low ionic mobilities within the solid polymer. To achieve higher energy and power densities (e.g. per unit area of electrode) rather thicker layers of electroactive material are required. Recently [10–12], it has been shown how significant improvements in performance can be achieved by using aqueous electrolytes and hybrid electrode materials containing combinations of pPy and carbon nanotubes. The advantage of the electroactive polymer would then be the combination of high specific capacity (ca. $160\,F\,g^{-1}$) with rapid device response. This is the approach followed in this paper.
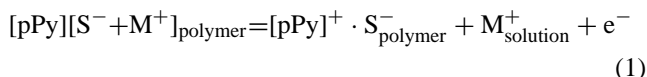
Our attention has been drawn to recent work by Naoi and co-workers [13,14] in which they have explored the use of surfactant anions as 'permanent' dopants, which because of their size are immobilised within the polymer matrix. The subsequent process of doping can then proceed by the ejection of cations followed by the insertion of additional anions from the electrolyte solution.

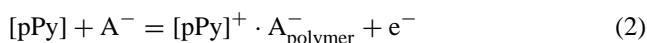* Corresponding author. Tel.: +44-1224-272905;
fax: +44-1224-272921.
E-mail address: m.d.ingram@abdn.ac.uk (M.D. Ingram).

The charging processes in this 'dual mode' pattern of behaviour involves

$$[pPy][S^- + M^+]_{polymer} = [pPy]^+ \cdot S^-_{polymer} + M^+_{solution} + e^- \tag{1}$$

followed by

$$[pPy] + A^- = [pPy]^+ \cdot A^-_{polymer} + e^- \tag{2}$$

where S^- is a surfactant anion lodged in the polymer, and M^+ and A^- are ions present in the electrolyte solution used in the subsequent charge/discharge experiments.

The outcome is that there can be a switch between mechanisms (1) and (2), depending on the redox state of the material, see also references [15–18]. Naoi and co-workers suggested the attractive possibility [13,14] that the redox processes may be speeded up in this way, especially if cations move faster than anions. Thus, they argued that 'secondary' doping, i.e. reaction (1), could be more effective than 'primary' anion doping by reaction (2).

Recently, we have described a range of self-doping strategies for achieving fast response with pPy electrodes in both PC-based and aqueous electrolytes [19,20]. The most encouraging results were obtained where the pPy was deposited in the presence of di- and tri-sulfonated aromatic compounds. We proposed that the improved behaviour of these materials be attributed to a *ladder doping* mechanism, whereby channels are created within the structure to allow for the entry of ions and water molecules from the surrounding electrolyte.

The essential idea is illustrated in Fig. 1. The heterocyclic pyrrole rings are represented by ellipsoids and the polysulfonated hydrocarbon anions by parallelograms. When the film is in an oxidised state, the anions form bridges between positively charged neighbouring polymeric chains. In this way, the anions act like rungs in a ladder, and in so
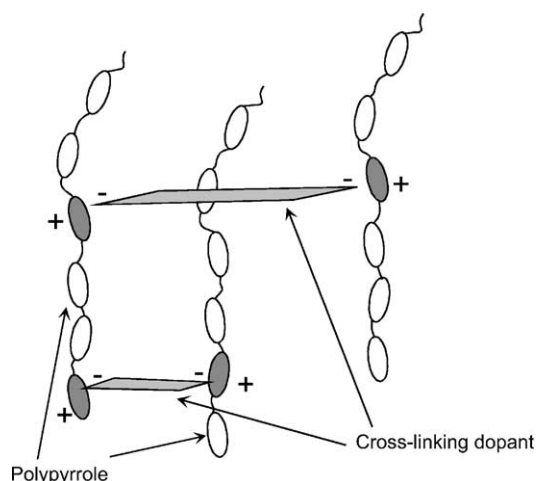

Fig. 1. The 'ladder doping' mechanism in pPy crosslinked by polysulfonated aromatic hydrocarbons. The shaded ellipsoids show positions of positive holes; the parallelograms indicate bridging aromatic anions (the rungs on the ladder).

doing keep open the channels in which fast ionic motion can occurs.

In the present paper, we discuss in more detail the way ladder doping operates, and the suitability of these materials for supercapacitor application.

2. Experimental

The electrodeposition of polymer and its subsequent characterisation by cyclic voltammetry (CV) were performed with an Autolab PGSTAT20 Eco Chemie supplied by Windsor Scientific (UK). Normally, polypyrrole was deposited potentiostatically (0.8 V versus a commercial Ag/AgCl electrode) from aqueous solutions that are 0.1 M with respect to both pyrrole and the sodium sulfonate salt, onto a 2 mm diameter platinum microelectrode (BAS, USA). A large platinum flag served as the counter electrode. In subsequent CV experiments, a silver flag or the Ag/AgCl electrode acted as the reference electrode for propylene carbonate (PC) or aqueous, respectively. A Luggin capillary minimised the IR drop between the working and reference electrodes. In each case, a quantity of electricity of 94.3 mC (equivalent to $3\,C\,cm^{-2}$) was used during the electrodeposition process, yielding films typically 10 μm in thickness.

In the preparation of electrodes for the two-electrode cells used in preliminary supercapacitor trials, a charge of 10 C was used to deposit pPy under correspondingly potentiostatic conditions onto carbon paper (PE715, SIGRI, Germany) or platinum flag electrodes (1 cm × 1 cm on each side). Cyclic voltammetry was performed in appropriate salt solutions (in the absence of pPy). When the 'toy' supercapacitor was tested, one electrode served as both reference and counter electrodes simultaneously.

All chemicals were supplied by Aldrich, apart from the $NaClO_4$, $MgCl_2$ and KCl, which were supplied by Merck. Sulfonated hydrocarbon salts under investigation included the sodium salts of: 1,3-benzenedisulfonic acid (BDS), 1-naphthalenesulfonic acid (NMS), 2,6-naphthalenedisulfonic acid (NDS), 1,3,6-naphthalenetrisulfonic acid (NTS) and anthraquinone-2,6-disulfonic acid (ADS).

3. Results

3.1. Choice of water as solvent

The first step was to decide if the electrodes were to be used in aqueous or nonaqueous environments. Fig. 2 shows CVs obtained at sweep rates of $10\,mV\,s^{-1}$ for pPy-NDS-doped electrodes, in 0.5 M solutions of $NaClO_4$ in propylene carbonate (PC) and water, respectively. Clearly, the electrode response is orders of magnitude better in water. A well-defined capacitive behaviour is indicated in the latter case by a 'box-like' trace extending from -0.5 to $+0.3$ V. All the subsequent discussion is focused on the behaviour in aqueous systems.
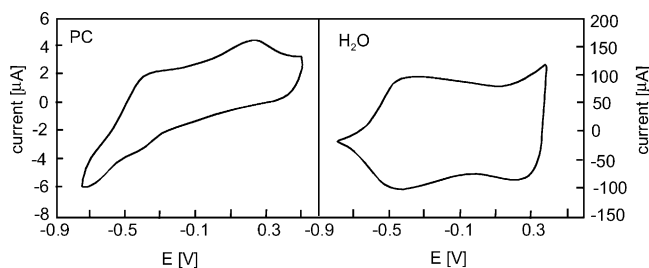
Fig. 2. Cyclic voltammograms for an NDS (2,6-naphthalenedisulfonate)-doped pPy electrode obtained in solutions of NaClO$_4$ in propylene carbonate and aqueous solution. (See text for details.)

The capacitance of the pPy-NDS electrode can be evaluated from the current (either anodic or cathodic) flowing in this 'constant current' region. Thus, from the right hand graph, one obtains: $C = I/(\mathrm{d}V/\mathrm{d}t) \approx (70 \times 10^{-6})/(10 \times 10^{-3}) = 7\,\mathrm{mF}$. (It is not realistic to make a comparable calculation for the PC-based electrolyte because there is so little in the way of capacitive behaviour, but the corresponding value would be much smaller (ca. 0.2 mF).)

3.2. Choice of electrolyte

Fig. 3 shows how the voltammetric behaviour of the pPy-NDS electrode compares in three aqueous electrolytes: 0.1 M NDS, 0.1 M MgCl$_2$ and 0.1 M NaClO$_4$, cycled at 10 and 100 mV s^{-1}, respectively.

Looking first at the traces obtained at 10 mV s^{-1}, one sees that in the NDS solution the only significant electrochemical process involves quasi-reversible cathodic/anodic 'peaks' appearing close to −0.5 V with respect to the Ag/AgCl electrode. These peaks can be assigned with some confidence to the reversible insertion/ejection of Na$^+$ ions, reaction (1), see reference [16] for example. Anodic and cathodic currents at more positive potentials are by comparison very small. There is very little capacitive behaviour.

In the case of MgCl$_2$, the corresponding cathodic/anodic 'peaks' are shifted to more positive potentials (ca. 0.0 V), and now appreciable capacitive behaviour is seen at more positive potentials. Almost certainly, see reference [16] again, one can conclude that cations are not involved in the redox behaviour. Instead, anionic doping/dedoping processes dominate the entire electrochemical response.

The behaviour of NaClO$_4$ seems to combine favourable features present in the other systems. Thus, the electrochemistry commences with cation-based processes at −0.5 V, and capacitive behaviour, possibly involving cations and anions continues up to +0.3 V. Moreover, the shape of the cyclic voltammograms is preserved much better at a higher sweep rate of 100 mV s^{-1} than it is for either of the other electrolytes. Increasing the sweep rate leads to an increase in the capacitive current from approximately 70 to 700 μA, a result consistent with a constant capacitance of 7 mF.

We conclude that a combined cation–anion response is necessary for ensuring the proper functioning of the sulfonate-doped pPy electrodes. This happens very efficiently with NaClO$_4$ and very similar behaviour is found with other common salt solutions such as LiCl, NaCl, KCl, NaNO$_3$ and KNO$_3$. Change of concentration does not seem to have a strong effect.

This essentially *dual mode* behaviour does not occur, however, if divalent cations or large surfactant anions are present, possibly because Mg^{2+} ions are too strongly hydrated to leave the aqueous phase and enter the polymer, and because the NDS^{2-} anions are too bulky to enter or leave the film once it has been deposited. Of course, this latter point forms the basis of the ladder-doping concept.

3.3. Thickness of the elecrodeposited film

Scanning electron micrographs (SEMs) are shown in Fig. 4 for films of NMS, BDS, ADS and NTS-doped pPy deposited onto a Pt substrate. The polymer film was first removed from the electrode with a doctor blade and then attached to a conducting metallic stub with silver paint so that the cross section is facing upwards, and finally coated with evaporated gold to prevent surface charging. The films exhibit a variety of external morphologies, becoming somewhat 'fluffier' and possibly more porous, with increasing numbers of sulfonate groups per aromatic anion. However, in each case the films were approximately 10 μm thick.

Except for the monosubstituted NMS, all these materials behave electrochemically very like the NDS material described above, but slightly higher capacitances and more 'reversible' behaviours are encountered with increasing numbers of sulfonate groups. It may not be a coincidence
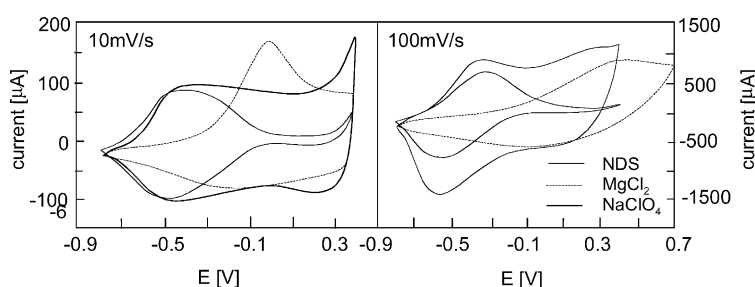

Fig. 3. Cyclic voltammograms of an NDS-doped pPy electrode in aqueous solutions of NDS, MgCl$_2$ and NaClO$_4$, respectively.
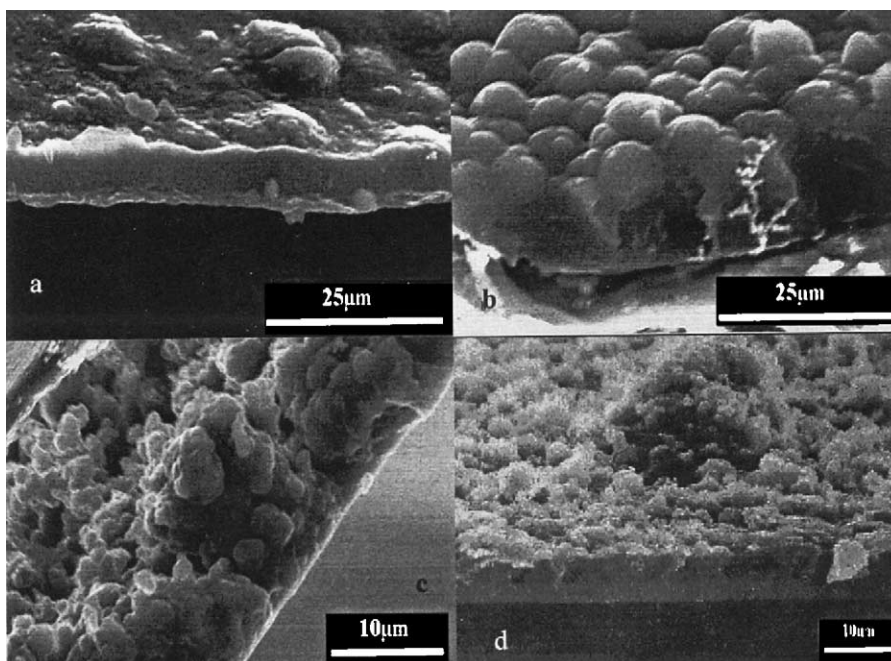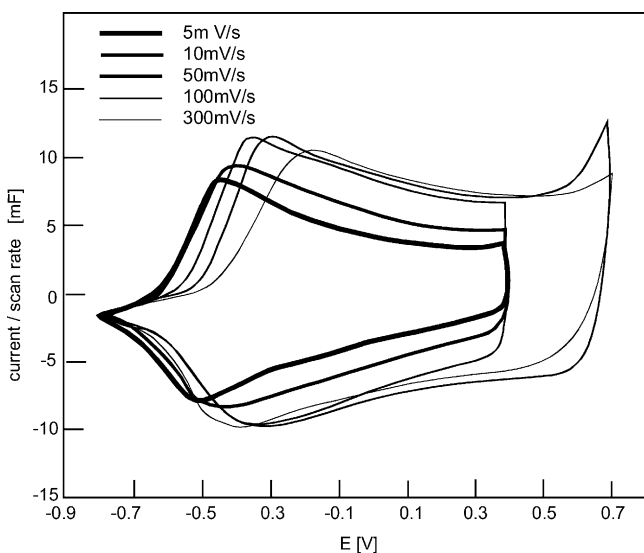

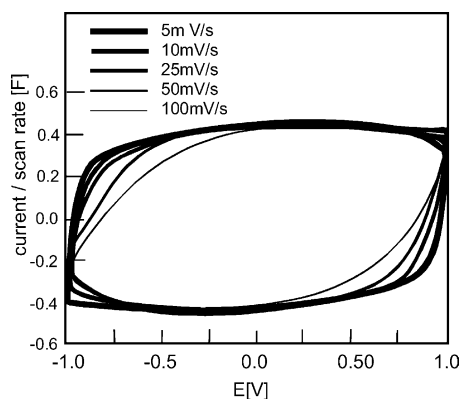Fig. 6. Cyclic voltammograms for a two-electrode cell, formed by two NTS-doped pPy electrodes (on Pt flags) in 2 M KCl at varying sweep rates. Note that the scaled currents (expressed in F) are essentially independent of sweep rate.

3.5. Testing of 'toy' supercapacitors

To explore the possibility of 'scaling up' this electrode concept for energy storage purposes, a simple capacitor cell was constructed (a) with larger Pt and (b) carbon paper electrodes (each 1 cm × 1 cm), placed approximately 2 cm apart in 2.0 M KCl solution. The electrodes had been plated on both sides with pPy/NTS, receiving a total charge of 10 C. The potential difference across the simple supercapacitor was cycled repetitively from −1.00 to +1.00 V at various sweep rates.

Fig. 6 shows the behaviour of the Pt-based cell. In contrast to the systematic variations obtained in the conventional three-electrode cell, the capacitance *remains constant* at 0.4 F over a range of sweep rates varying from 5 to 100 mV s^{-1}. Bearing in mind that for two capacitances in series, $1/C = 1/C_1 + 1/C_2$, and assuming that these two electrodes will have the same capacitance, the capacitance *for each electrode* is 0.8 F. Since the total area of both sides of each electrode is 2 cm^2, the specific capacitance of the material itself is 0.4 F cm^{-2}.

For the carbon-based capacitor, a similar capacitance (ca. 4 mF) was obtained, which again did not vary with sweep rate. The capacitance did however vary almost linearly with both the quantity of electricity and the amount of pPy deposited. When the charge was 10 C, the weight of polymer deposited was 5.2 mg.

This figure is somewhat larger than that based on Faraday's law (ca. 3 mg) even when the weight of dopant anion (naphthalene trisulfonate) is considered. The implication must be that additional sodium poysulfonate is incorporated during electrodeposition of the polymer. The figure corresponds to a specific capacitance of 0.8 F per 0.005 g, or 160 F g^{-1}, which is close to what is commonly quoted for pPy in the literature. In any case, for comparative purposes, the specific capacitance should be based on actual weights of electrode material and not on calculated values.

4. Discussion

The main result to emerge is the confirmation of the earlier claim by Naoi and co-workers [14] that the performance of pPy electrodes is improved by the inclusion of polysulfonated organic anions during the electrodeposition process. We further show that the improvement in supercapacitor behaviour is seen only when 'dual mode' behaviour, i.e. when sequential doping with both cations and anions is allowed.

This complexity in the charge–discharge processes is well illustrated by the differing dependences of the electrode capacitance on sweep rate in three- and two-electrode cells, see Figs. 5 and 6, respectively. In the first case, the capacitance increases with increasing sweep rate; in the second there is no change.

We can account for this difference in terms of the ladder-doping mechanism, which is shown schematically in Fig. 1. Thus we argue that the 'rungs of the ladder' will be held in place only when the polymer is positively charged. Thus, when the charges on the polymer disappear, the anions will then be then free to reorient themselves and to 'pair off' with incoming cations. We now further suggest that if the polymer is left uncharged for some time, the ladder structure may collapse leading to the disappearance of the conducting channels.

Various kinds of structural relaxation are known to occur in pPy, see for example references [21,22], and they give rise to a variety of 'history effects'. In the present context, it would seem that rapid cycling of the NTS-doped electrode in the three-electrode cell leaves insufficient time for the structural collapse to occur, and thus the open structure is retained which is necessary for fast ion migration within the polymer. The time required for such a relaxation to occur could be the origin of the improvement in behaviour seen at fast scan rates, Fig. 5.

Alternatively, the structural collapse could be averted altogether if the polymer is never fully discharged. We think this could explain the behaviour seen in Fig. 6. Thus, each electrode in the test cell might be swept from approximately −0.5 to +0.5 V (on the Ag/AgCl reference scale used in Fig. 5) and thus neither would become completely discharged. This would also account for the large specific capacitance observed in the test capacitors.

The apparent deterioration in cell behaviour, which is seen at high sweep rates in Fig. 6, is almost certainly a consequence of the non-optimised (i.e. poor) cell design. The fact that the capacitance always reaches the same value, regardless of sweep rate (and hence of charging current), implies that the pPy on both sides of the Pt electrodes and on all the C fibres are being charged and discharged during each cycle. In order for the maximum current to be reached, however, charged polymer must first build up on the electrode surfaces that are closest to each other. This in turn establishes a 'back emf', which opposes this tendency to focus and thus spreads the current uniformly over all the exposed surfaces. With appropriate development and a cell design that

eliminates variations in the length of the conducting pathways, response rates of up to $300\,mV\,s^{-1}$, corresponding to charge or discharge times of 3 s should easily be achieved.

In conclusion, we suggest that the ladder-doping concept offers a promising route to the preparation of novel electroactive polymers for use in high-power electrochemical supercapacitors. Although these materials function at present only in aqueous systems, and are therefore limited to working between 0 and 1 V, the high rates of charge and discharge obtainable will ensure the achievement of the high-power densities needed for use in hybrid electric vehicles.

Acknowledgements

References

[1] B.E. Conway, Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications, Kluwer Academic/Plenum, New York, 1999.
[2] A. Burke, J. Power Sour. 91 (2000) 3748;
A. Burke, J. Power Sour. 91 (1998) 1601.
[3] A. Rudge, I. Raistrick, S. Gottesfeld, J.P. Ferraris, Electrochim. Acta 39 (1994) 273.
[4] A. Clemente, S. Panero, E. Spila, B. Scrosati, Solid State Ionics 85 (1996) 273.
[5] S. Panero, A. Clemente, E. Spila, Solid State Ionics 86–88 (1996) 1285.
[6] M. Mastragostino, C. Arbizzani, F. Soavi, Solid State Ionics 148 (2002) 493.
[7] C.C. Hu, X.X. Lin, J. Electrochem. Soc. 149 (2002) A1049.
[8] A. Laforgue, et al., J. Electrochem. Soc. 150 (2003) A645.
[9] M.D. Ingram, A.J. Pappin, F. Delalande, D. Poupard, G. Terzouli, Electrochim. Acta 48 (1998) 1601.
[10] E. Frackowiak, K. Jurewicz, S. Delpeux, V. Bertagna, F. Beguin, S. Bonnamy, Mol. Cryst. 387 (2002) 297.
[11] M. Hughes, G.Z. Chen, M.S.P. Shaffer, D.J. Fray, A.H. Windle, Chem. Mater. 14 (2002) 1610.
[12] K.H. An, K.K. Jeon, J.K. Heo, S.C. Lim, D.J. Bae, Y.H. Lee, J. Electrochem. Soc. 149 (2002) A1058.
[13] K. Naoi, Y. Oura, M. Maeda, S. Nakamura, J. Electrochem. Soc. 142 (1995) 417.
[14] S. Suematsu, Y. Oura, H. Tsujimoto, H. Kanno, K. Naoi, Electrochim. Acta 45 (2000) 3813.
[15] K. West, M.A. Careem, S. Skaarup, Solid State Ionics 60 (1993) 153.
[16] T. Shimidzu, A. Ohtani, K. Honda, J. Chem. Soc. Jpn. 61 (1988) 2885.
[17] C. Zhong, K. Doblhofer, Electrochim. Acta 35 (1990) 1971.
[18] S. Skaarup, et al., Solid State Ionics 159 (2003) 143.
[19] M.D. Ingram, H. Staesche, K.S. Ryder, Solid State Ionics, in press.
[20] H. Staesche, PhD Thesis, University of Aberdeen, 2002.
[21] R. Hillman, S. Bruckenstein, J. Chem. Soc., Faraday Trans. 89 (1993) 3779.
[22] S. Bruckenstein, A.R. Hillman, J. Phys. Chem. B 102 (2000) 10826.