JOURNAL OF APPLIED ELECTROCHEMISTRY **22** (1992) 512–516

A polyaniline and Nafion® composite film as a rechargeable battery

N. LI, J. Y. LEE, L. H. ONG

Department of Chemical Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 0511

Received 1 August 1991; revised 1 October 1991

The charge–discharge characteristics of polyaniline (PAn)–Nafion®–PAn composite films used as rechargeable batteries were investigated. The batteries were formed chemically by sandwiching Nafion® between two thin layers of PAn–Nafion® composite in equilibrium with various electrolytes. It was found that cells with $LiClO_4$ in propylene carbonate as electrolyte showed the highest capacity. The charge and discharge performance of the battery was almost independent of the choice of anions but was significantly affected by cation size. This may indicate that the insertion or removal of charge-compensating electrolyte cations from the composite layer was responsible for the redox of PAn during the charge and discharge cycles.

1. Introduction

Polyaniline (PAn) has been known as a promising electroactive polymer for secondary batteries [1–3]. When it is used as the active electrode, PAn may either be electrochemically deposited onto a conductive substrate as a thin film [1, 3] or be chemically synthesized in powder form and then mixed with a suitable binder to form a sheet or pasted electrode [3]. In this paper, the preparation of a PAn–Nafion®–PAn composite film as a rechargeable battery will be described.* The composite film has thin layers of PAn concentrated on both sides of Nafion® in equilibrium with an aqueous or non-aqueous electrolyte.

Nafion® is a perfluorosulphonic acid cation exchange membrane. According to a model proposed by Gierke and Hsu [4], it consists of a network of hydrophillic clusters in the hydrophobic fluorocarbon matrix. The clusters contain sulphonates and counter ions and are interconnected by short channels. Detailed studies on the structural properties of Nafion® membranes can be found elsewhere [5]. Honda and Hayashi [6] have prepared a Prussian Blue (PB)–Nafion® composite film as a solid state rechargeable battery. Thin layers of PB were overlaid on both sides of Nafion® which also served as the intervening electrolyte. Good performance of the PB–Nafion® battery and high durability of the electroactive materials were reported. Recently there are also reports on the preparation of polypyrrole (PPy)–Nafion® and PAn–Nafion® composites by chemical oxidation of pyrrole or aniline on the cation exchange site of Nafion® [7], and by electrochemical polymerization of the monomers in Nafion® gel [8–10]. The composite has remarkably improved the mechanical properties of the brittle electroactive polymers without any significant reduction in their conductivity. Another useful feature of the composite film is the assurance of a good contact between the electrode active material and the electrolyte. Meanwhile, it has also been suggested that the sulphonate group of Nafion® is involved in the doping of PAn and PPy in the composite [7–10].

It is easy to form a thin layer of PAn–Nafion® composite in the surface region of Nafion® by chemical methods [7]. A rechargeable battery similar to the PB–Nafion® battery investigated by Honda and Hayashi [6] can then be formed by sandwiching Nafion® between two thin layers of PAn–Nafion® composite. The following discussions will focus on the preparation of the rechargeable PAn–Nafion® battery and the evaluation of its performance.

2. Experimental details

Aldrich Nafion® 117 membrane (0.178 mm in thickness) was cut into square pieces of dimensions 15.5 mm × 15.5 mm and thoroughly washed with dilute $HClO_4$. The Nafion® film was then equilibrated in 1 M $Fe(ClO_4)_3$ aqueous solution containing 0.5 M $HClO_4$ for 1 h. The Fe(III) exchanged Nafion® was rinsed with distilled water and equilibrated in 1 M aniline in 1 M $HClO_4$ solution for another hour. The polymerization of aniline by the Fe(III) ions occurred quickly inside the membrane and the film became dark green. The above treatment was repeated several times so that more PAn could be incorporated into the Nafion® film. The optimal number of treatments has, however, been found to be four, as will be discussed later. The resulting PAn–Nafion® composite film was further washed with distilled water and completely dried under vacuum for at least 48 h before it was

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* The use of the word 'rechargeable battery' is preferred over 'supercapacitor' here. Nafion® is used to form an 'intercalation' compound with PAn, its functionality is therefore different from its role as a binder for the dispersed electroactive phase in supercapacitors [17]. The significant deviations from linearity in most of the charging–discharging curves also indicate the importance of bulk processes in relation to surface processes in the redox reactions.

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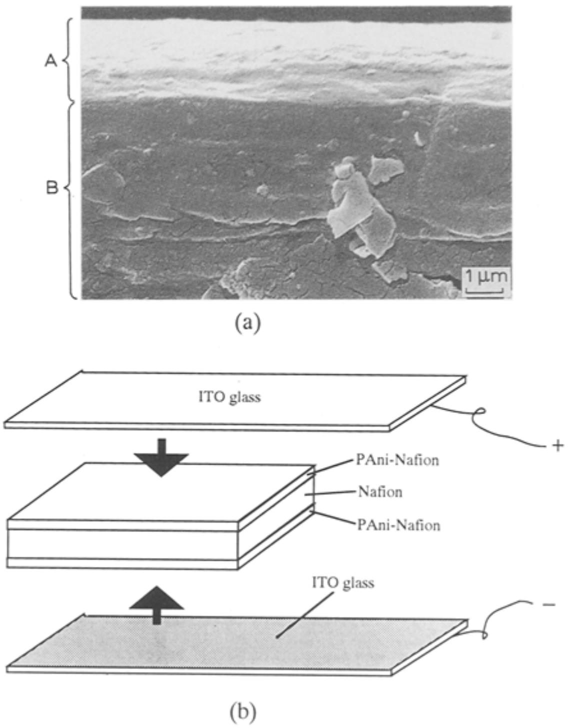
immersed in an appropriate aqueous or non-aqueous electrolyte for two days to exchange the Fe(III) remaining inside the film with the cation ions in the solution. Following this treatment, the composite was trimmed to a 15 mm × 15 mm square film. The battery was then fabricated by sandwiching the PAn–Nafion®–PAn composite film between two indium tin oxide (ITO) coated glass plates as current collectors. The positive and negative electrodes of the battery can be arbitrarily chosen as they are of the same material.

Cyclic voltammograms (CV) were obtained for a Nafion® coated electrode on which PAn was electrochemically deposited. The preparation of this electrode was as follows: a 5 wt % solution of Aldrich Nafion® 117 in a mixture of alcohols and water was uniformly spread onto a stainless steel substrate and dried in air for a week. The electropolymerization of aniline was carried out at 0.9 V against Ag/AgCl in a 0.5 M aniline solution in 1 M $HClO_4$. The resulting PAn–Nafion® electrode was then washed with distilled water and dried completely. The electrode was preconditioned at -0.2 V against Ag/AgCl for 30 min before each CV run, which ramped the potential range of -0.2 to $+0.6$ V (against Ag/AgCl) at 10 mV s^{-1}.

AR grade aniline was redistilled before use. All other chemicals were of reagent grade and sufficiently dried whenever propylene carbonate (PC) was used as a solvent. Battery charge and discharge tests were carried out on an EG&G Model 362 potentiostat with a Rikadenki multi-pen recorder, whereas an EG&G Model 270 was used for electropolymerization and CV measurements.

3. Experimental results

Scanning electron microscopy (Fig. 1a) shows that PAn is mostly concentrated in the surface region of the Nafion® film (Region A). The structure of the composite film can be illustrated schematically in Fig. 1b. The PAn–Nafion® composite was detected as a uniform layer of thickness about 2.3 μm. The formation of a composite layer only in the surface region may be caused by a slow diffusion of aniline monomers into the Nafion® matrix compared to a relatively fast polymerization of aniline by the oxidizing Fe(III) sites in the film. The PAn thus formed is likely to be entangled with the ionomer chains of Nafion®, thereby constricting the interconnecting channels in the Nafion® matrix and preventing the diffusing aniline from accessing the deeper film interior. In this case, the following polymerization is limited mostly to a thin layer beneath the surface of the film. Indeed, the charge and discharge curves of PAn–Nafion® batteries did not seem to change significantly after four repetitions of the Fe(III) exchange and polymerization sequence.



(a)

(b)

Fig. 1. (a) Scanning electron micrograph of PAn–Nafion–PAn composite film. Region A: PAn-Nafion composite layer; region B: Nafion. (b) Schematic diagram of the rechargeable PAn-Nafion battery.

The charge and discharge performance of PAn–Nafion® batteries in different electrolytes is shown in Figs 2 and 3. With the exception of the cells using $NaClO_4$ in PC, non-aqueous cells generally perform better in terms of capacity, cell voltage and coulombic efficiency. At the fixed charging rate of 20 μA (Fig. 2a), the cell using $LiClO_4$ in PC has the highest capacity. The capacities of the cells with tetraethylammonium perchlorate ($(C_2H_5)_4NClO_4$) and tetraethylammonium (toluene-4-sulphonate) ($(C_2H_5)_4N(CH_3C_6H_4SO_3)$) in PC as electrolytes are almost independent of the choice of anions. The effect of charging current on capacity can be seen in Fig. 2b. A nearly 20% decrease in capacity was noted when the charging current was increased from 20 to 50 μA. Such observation is usually indicative of a limitation by transport processes in battery operation.

The cells were charged to a potential of 0.5 V followed by an immediate discharge at the same rates. Figures 3a and b are the resulting discharge curves showing the effect of electrolyte and charging current respectively. It is evident that the coulombic efficiencies are almost 100%. This is not true for cells formed with an aqueous electrolyte of $LiClO_4$ or $NaClO_4$ in PC for which an '*IR* loss' was also observed immediately upon discharge, in addition to the fact that they were not normally able to charge up to 0.5 V, as with other cells, in the first place.

The electrochemical behaviour of the battery may be deduced from a composite electrode made from PAn and Nafion® although the electrochemical environment in both cases may not be exactly identical. Indeed, the composite PAn–Nafion® electrode is best visualized as a PAn–Nafion® battery cut in the middle. The composite electrode has the characteristic dark green colour of the doped emeraldine state [11]. Typical cyclic voltammograms of such an electrode in electrolytes the same as used in the battery preparation are given in Fig. 4. It can be seen that the

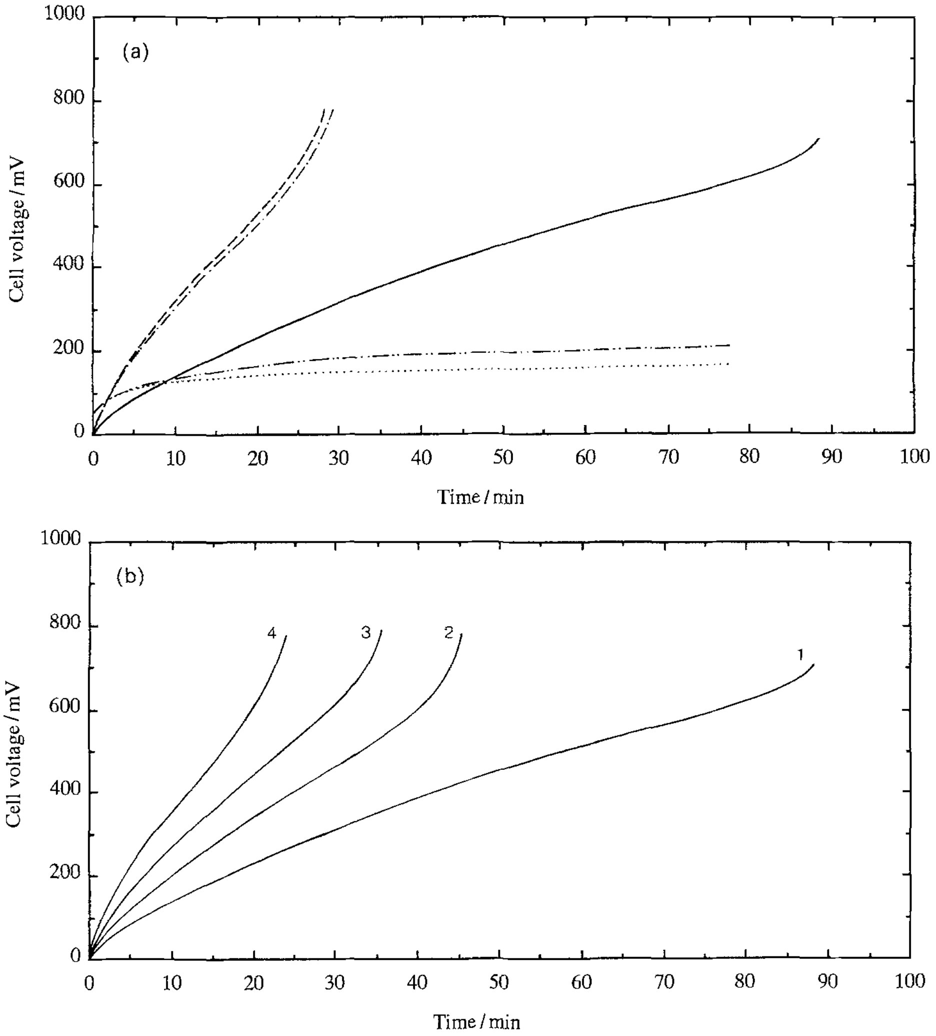


Fig. 2. (a) Charging of PAn–Nafion composite batteries at 20 μA. Electrolytes: (– – –) 1 M tetraethylammonium (toluene-4-sulphonate) [$(C_2H_5)_4N(CH_3C_6H_4SO_3)$] in PC; (–·–·–·–) 1 M tetraethylammonium perchlorate [$(C_2H_5)_4NClO_4$] in PC; (——) 1 M $LiClO_4$ in PC; (—··—) aqueous 1 M $LiClO_4$ solution at pH 1; (····) 1 M $NaClO_4$ in PC. (b) Charging of PAn–Nafion batteries in 1 M $LiClO_4$ in PC at different rates. Charging current/μA: (1) 20, (2) 30, (3) 40 and (4) 50.

potentials of the anodic and cathodic peaks are dependent on the cation size but the nature of the anions has very little effect on the shape of the voltammograms. This is almost a natural consequence for the use of Nafion® as will be discussed fully in the next section.

4. Discussion

The redox reactions of PAn have been extensively studied in recent years [11–13]. It is generally believed that proton addition/elimination in conjunction with anion doping/dedoping occur during the charge and discharge of a PAn electrode in aqueous media [1, 11]. In non-aqueous electrolyte, however, there is evidence that only the doping and dedoping of anions occurs. In the case of PAn–Nafion® composite electrodes, PAn cation is mostly balanced by the immobile perfluorosulphonate anions of the Nafion® matrix [8]. As the doping and dedoping of anions are unlikely to occur, in this case, the injection or removal of charge at the electrodes during battery operation is supported mainly by the movement of cations within the composite layer.

PAn is easiest prepared in the emeraldine state and, in such a state, it can be reduced to leucoemeraldine or oxidized to nigraniline or pernigraniline. The reversibility of the reduction reaction is believed to be better than that of oxidation. It is therefore conceivable, at least in principle, to devise an all-PAn cell using the redox of PAn as a source of energy. Such a cell will contain initially two PAn electrodes in the emeraldine state which, upon charging, separate into a leucoemeraldine electrode and an oxidized emeraldine electrode respectively. Based on the cyclic voltammetry studies of Huang [11] and Okabayashi [12], the difference in potentials between leucoemeraldine–emeraldine and emeraldine-oxidized-emeraldine transitions is approximately 0.55–0.6 V in aqueous and non-aqueous electrolytes respectively. This potential difference is very close to the o.c.v. of 0.53 V (Fig. 3) reported here. Therefore, when an all-PAn battery is charged, emeraldine is oxidized at the positive electrode and reduced at the negative electrode. The processes are reversed during discharge and the electrodes are returned to the emeraldine state. The property of Nafion® to limit deposition of PAn to its surface region is exploited here to simplify the construction of the all-PAn cells. In this case both electrodes and the intervening electrolyte are formed in one step.

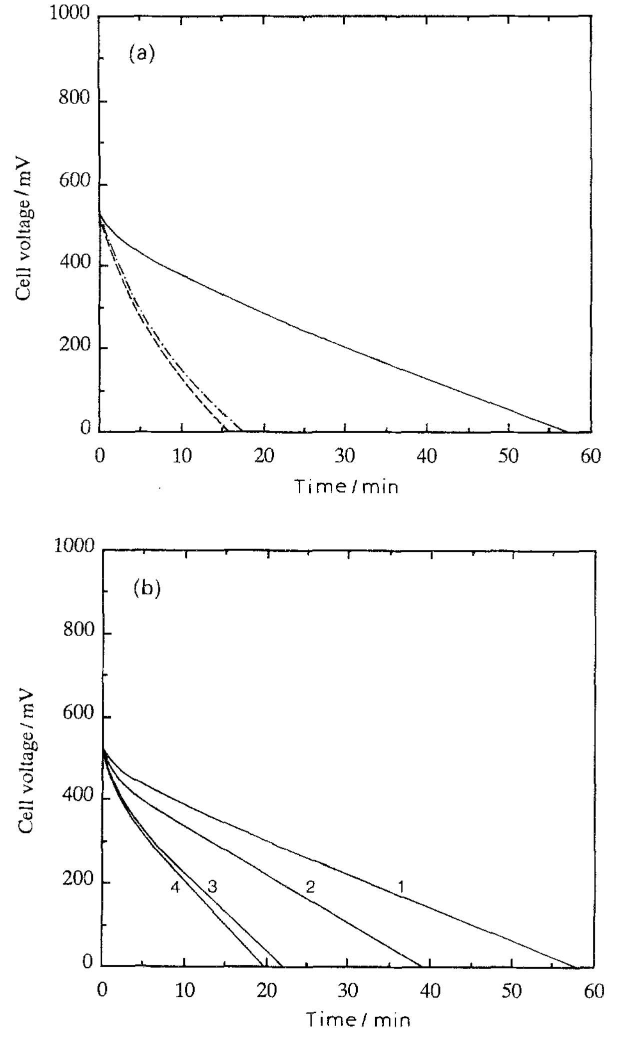


Fig. 3. (a) Discharge curves of PAn–Nafion composite batteries at 20 μA. Electrolytes: (– – –) 1 M $(C_2H_5)_4N(CH_3C_6H_4SO_3)$ in PC; (–·–·–) 1 M $(C_2H_5)_4NClO_4$ in PC; (——) 1 M $LiClO_4$ in PC. (b) Discharge curves of PAn–Nafion composite batteries in 1 M $LiClO_4$ in PC. Discharging current/μA: (1) 20, (2) 30, (3) 40 and (4) 50.

The composite electrodes used here are generically the same as the polypyrrole-polyanion (PPy/PA) electrodes in rechargeable batteries [15, 16], where the incorporated macromolecular PA as a dopant was not released during the reduction of the PPy/PA due to its large molecular size, and the penetration of electrolyte cations into the composite matrix maintained the electroneutrality in the electrode film. Nafion® as a cation exchange membrane should be even more effective to exclude anions from the composite layer and render anion migration insignificant in the charge and discharge of PAn electrodes. This is supported by the near coincidence of the charge and discharge curves of the batteries using $(C_2H_5)_4NClO_4$ and $(C_2H_5)_4N(CH_3C_6H_4SO_3)$ in PC in Fig. 3 where the only difference between them is in the anion size. Generally the ohmic loss of non-aqueous PAn–Nafion® cells is negligible. However, a large polarization is observed with large electrolyte cations, resulting in a lower cell capacity. Cyclic voltammograms of PAn–Nafion® composite electrodes with large electrolyte cations also displayed a larger separation between the anodic and cathodic peaks as a result of the anodic peak being shifted more positively and the cathodic peak more negatively (Fig. 4). The increased irreversibility of large electrolyte cations can be partly explained by the hindered movement of the solvated cations within the Nafion® matrix, although a measurement of the ionic conductivities of PC solutions of $(C_2H_5)_4NClO_4$ and $NaClO_4$ gave very comparable values of (11.3 mS cm^{-1} and 10.9 mS cm^{-1}, respectively). PC solutions of large electrolyte cations $[(C_2H_5)_4N^+]$ were found to swell Nafion® films substantially (22.9%) while the small electrolyte cations (Na^+) could only do so marginally (3.1%). It is undeniable that cations solvated by PC play an important role in breaking the coulombic attractions in the Nafion® matrix. However, the specific interactions between the solvated cations and the Nafion® structure cannot yet be identified from the experimental data. It can only be concluded that the most suitable electrolyte for the PAn–Nafion® composite battery according to our investigation is $LiClO_4$ in PC. In this connection we should also highlight the poor performance of the the aqueous based PAn–Nafion® (in $LiClO_4$) and the use of $NaClO_4$ electrolyte. These batteries have relatively large ohmic losses in addition to their inability to accept substantial charges. Perhaps the solvated cations involved in these formations

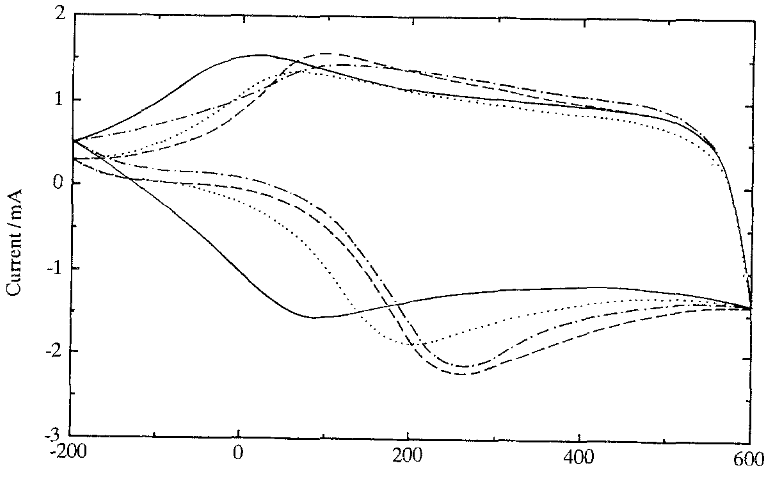


Fig. 4. Cyclic voltammograms of PAn–Nafion composite electrode in PC containing: (——) 1 M $NaClO_4$; (···) 1 M $LiClO_4$; (– – –) 1 M $(C_2H_5)_4NClO_4$; (–·–·–) 1 M $(C_2H_5)_4N(CH_3C_6H_4SO_3)$. Scan rate: 10 mV s^{-1}.

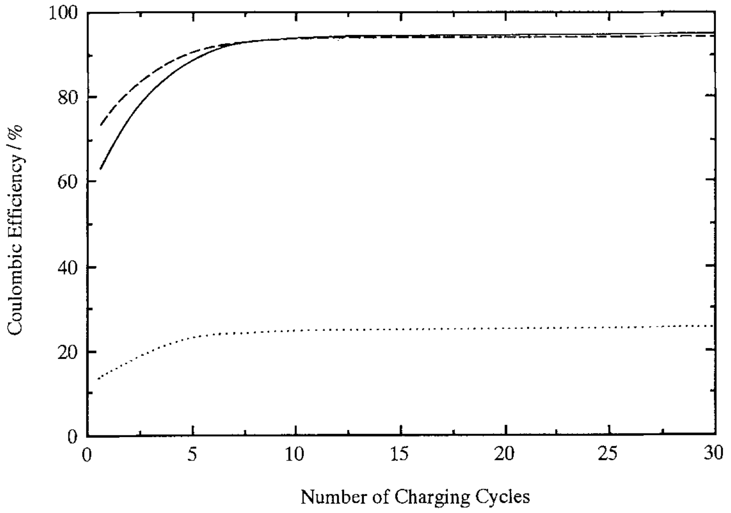


Fig. 5. Relationship between coulombic efficiency and number of charging/discharging cycles. Current: 10 μA. PC electrolyte: (——) 1 M $LiClO_4$; (– – –) 1 M $(C_2H_5)_4NClO_4$; (····) 1 M $NaClO_4$.

are less capable of disrupting the strong coulombic bonds in the Nafion® structure.

The coulombic efficiencies as determined from the ratios of discharging time to charging time for three different electrolytes, $(C_2H_5)_4NClO_4$, $LiClO_4$ and $NaClO_4$, are plotted against the number of cycles in Fig. 5. An efficiency of about 93% was obtained after six cycles when the first two electrolytes were used. The lower coulombic efficiency for the first few cycles of charging and discharging could be attributed to a poor electrical contact between the composite film and the ITO glass plates. Such contact was known to be quickly improved with repeated charging and discharging of the battery [6]. The coulombic efficiency for the $NaClO_4$ electrolyte remains lower for the same reasons as mentioned earlier. It was also found that the self-discharge of the composite electrodes was high (about 50% of the capacity was lost after 20 h in storage). We are currently investigating the reasons for such high rates of self-discharge inherent in polymer based electrodes.

5. Conclusions

An all-PAn rechargeable battery can be made in a single step by chemical polymerization of aniline onto the Nafion® film. The insertion or removal of charge-compensating electrolyte cations from the composite layer in support of the redox of PAn occurs during the charging and discharging cycles. Except for a relatively high self-discharging rate, the battery with the right choice of electrolyte cation can have a high durability due to the interlocked structure of the composite and a good coulombic efficiency.

Acknowledgements

The authors express their thanks to Mr S. K. Tung of the Materials Science Laboratory, Department of Mechanical Engineering, National University of Singapore for the SEM measurements.

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