A new polymer/polymer rechargeable battery: polyaniline/LiClO$_4$(MeCN)/poly-1-naphthol

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Abstract

Electrosynthesized dedoped polyaniline (anode) and doped poly-1-naphthol (cathode) were used as electrode materials in a new rechargeable battery containing lithium perchlorate and perchloric acid in methyl cyanide (MeCN) as the electrolyte. The cell gave an open-circuit potential (OCP) of 1.4 V, a specific capacity of 150 Ah kg^{-1} and an energy density of 113 W h kg^{-1} (at a 1.0 V cutoff). The cell lost ∼5% of its capacity after 1 week due to the self-discharge. The charging/discharging tests (0.0–1.4 V) showed a gradual decrease in capacity up to 15% after 100 cycles. An advantage of such battery is the high power density (∼9 kW kg^{-1} at OCP) because of the extended surface area of the polymer layer compared to the metal electrode.
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1. Introduction

Extensive research work has been focused on developing a light rechargeable battery, especially Li batteries with a new doped poly-1-naphthol (cathode) material, such as polyaniline [1–6], LiMnO$_4$ modified with polypyrrole [7,8], LiCoO$_2$ [9] and organic acceptors [10–12]. Search for a new electrosynthesized dedoped polyaniline (anode) material and an efficient polymer electrolyte is receiving attention too [13–18]. A main disadvantage of using metals, such as lithium, as electrode materials is the limitation imposed on the power density since the reaction layer is restricted to the apparent surface area of the electrode. On the other hand, conducting polymers, such as polyaniline and polypyrrole, are characterized by very high specific capacities because of their largely extended surface areas compared to the apparent surface area of the electrode and proposed as supercapacitors for this reason [19]. It is a fundamental advantage of using a metal/polymer or a polymer/polymer battery that may compensate for a lower cell voltage. A promising cathode material in methyl cyanide (MeCN) is poly-1-naphthol, with a high doping/dedoping potential, ∼1.4 V, a conductivity of 1–10 mS cm^{-1} and

specific capacity of 60 mF cm^{-3} [20–22]. In MeCN, the first doping/dedoping process of polyaniline occurs at a much lower potential, ∼0.2 V [23]. Thus, a rechargeable polymer/polymer cell, with an emf window of at least 1.3 V could be constructed from dedoped polyaniline (reduced form) as the anode and doped poly-1-naphthol (oxidized form) as the cathode. It is aimed in the present brief work to explore the feasibility of a proto-type cell of polyaniline/poly-1-naphthol in MeCN as a step towards an all-polymer rechargeable battery.

2. Experimental

The chemicals: 1-naphthol, aniline, methyl cyanide (MeCN), LiClO$_4$, HClO$_4$ and LiCl were analytical grade and used without further purification. A three-electrode cell, a potentiostat-galvanostat (EG & G PAR, Model 271A) and an X–Y recorder were employed for the preparation of the electrode materials and characterization of the proposed rechargeable cell. The working, counter and reference electrodes were, respectively, a Pt disk electrode (area = 0.169 cm^2), a Pt sheet (area = 2 cm × 2 cm) and a Ag/AgCl/0.1 M LiCl (in MeCN). All potentials are referred to the standard hydrogen electrode (SHE). Prior to experiments, the electrolytic cell was deaerated with pure N$_2$ gas for 15 min. All experiments were carried out a controlled

temperature of 25 ± 0.2 °C. The polymers were prepared by anodic polymerization of 0.1 M monomer (aniline and 1-naphthol) in MeCN containing 0.2 M LiClO$_4$. The potential was cycled between -0.4 and 1.0 V for polyaniline and between 0.0 and 1.4 V for 1-naphthol at a scan rate of 20 mV s^{-1}. The galvanic cell was composed of polyaniline and poly-1-naphthol layers deposed electrochemically by 100 cycles on two 100 nm-thick Pt films on glass (area of each electrode $= 10$ cm^2) and 0.2 M LiClO$_4$ + 0.01 M HClO$_4$ in MeCN as the electrolyte. The formation charges consumed in preparation of poly-1-naphthol and polyaniline layers were 4.6 and 5.2 C cm^{-2}, respectively. With a thickness/formation charge factor of 0.18 μm/mC cm^{-2} [20,21], the thickness of poly-1-naphthol layer was ~0.8 mm. Polyaniline layer thickness was estimated to be ~1.2 mm by weighing the layer and using a density of 1.4 g cm^{-3} for the electrochemically prepared polyaniline [24]. Few tests were made using thicker polymer layers obtained by potential cycling for 18 h, i.e. ~600 cycles, (~30 mm-thick poly-1-naphthol and ~35 mm-thick polyaniline). Before testing the cell performance, polyaniline was reduced at -0.3 V and poly-1-naphthol was oxidized at 1.4 V for 10 min.

3. Results and discussion

Fig. 1 shows cyclic voltammograms (CVs) for polyaniline and poly-1-naphthol in 0.2 M LiClO$_4$ in MeCN. Perchloric acid (0.01 M) was added in the case of polyaniline as a source of protons to stabilize the electroactivity of polyaniline. In the absence of HClO$_4$, the polyaniline performance deteriorated quickly. As can be seen, the redox peaks responsible for the oxidation (doping)/reduction (dedoping) of the two conducting polymers occur in different potential regions. This may be encouraging to suggest the application of polyaniline as an anode material and poly-1-naphthol as a

cathode material in a polymer/polymer rechargeable battery. The redox processes involved in the electroactivity of polyaniline and poly-1-naphthol, in the potential window shown in Fig. 1, are summarized in Fig. 2. Oxidation of polyaniline (leucoemeraldine form) in the potential region -0.4 to 0.7 V is accompanied by a substantial increase in conductivity due to the partial transformation of the amino linkages to imino linkage (emeraldine salt) and the formation of polarons and bipolarons [25]. At higher potentials >0.8 V, however, overoxidation of the emeraldine results in the formation of the full imino form (pernigraniline), with a substantial decrease in conductivity and a high susceptibility to hydrolysis and degradation [26]. Up to 1.5 V, only one pair of redox peaks could be distinguished for poly-1-naphthol due to the polaron formation (on oxidation)/consumption (on reduction).

To evaluated the maximum open-circuit potential (OCP) for the proposed cell: polyaniline (anode)/poly-1-naphthol (cathode), the electrode materials were preconditioned at different potentials before monitoring OCP of each electrode for several hours. The preconditioning potentials were selected in a way aimed to maximize the OCP of the proposed cell. As can be seen in Fig. 3, OCP changes rapidly at the beginning due to the self-discharge of the electrode materials before a quasi-steady OCP is reached, that is practically independent of the reconditioning potential. Maximum OCP for polyaniline and poly-1-naphthol of -0.1 and 1.3 V, respectively, could be obtained for several hours. Thus, an emf for the proposed cell of ~1.4 V could be reached. The made galvanic cell: polyaniline/0.2 M LiClO$_4$ + 0.01 M HClO$_4$ (MeCN)/poly-1-naphthol showed an emf of ~1.4 V after preconditioning (polyaniline at -0.3 V and poly-1-naphthol at 1.4 V) and gradual decrease with time to ~1.3 V after 1 week. Traces of O$_2$ and water in the electrolyte seem to be the reason of the OCP decay of the cell. It can be explained by the partial oxidation of polyaniline (discharging) on the expense of O$_2$ reduction.
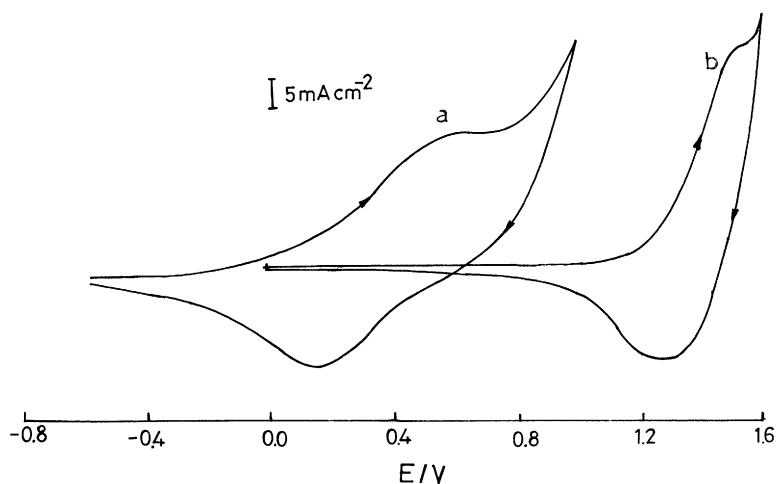

Fig. 1. CVs for polyaniline (a) and poly-1-naphthol (b) in 0.2 M LiClO$_4$ + 0.01 M HClO$_4$ in MeCN. Scan rate $= 20$ mV s^{-1}. The films were formed by 100 cycles.
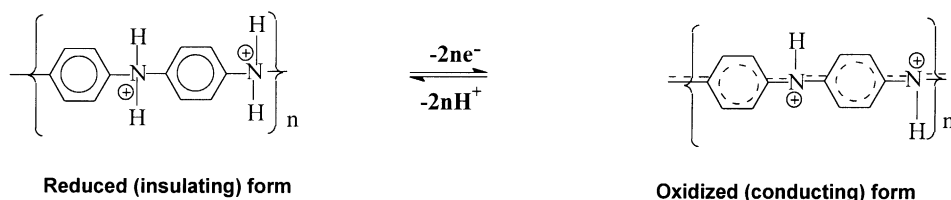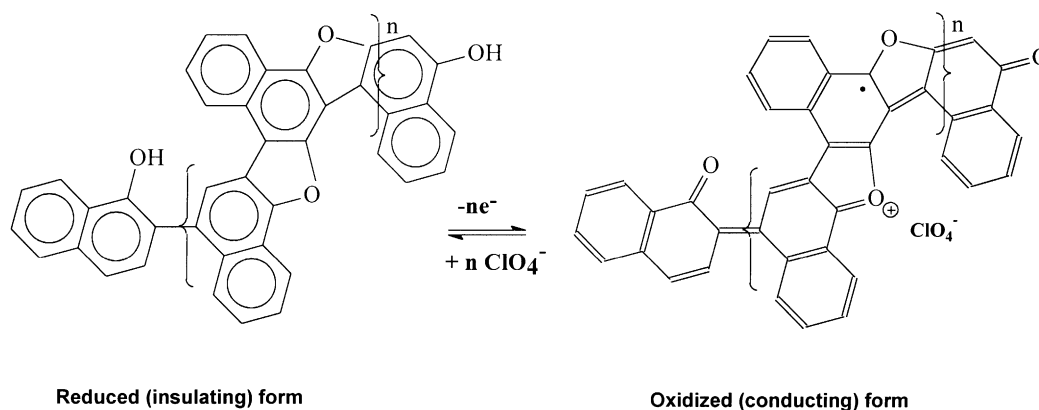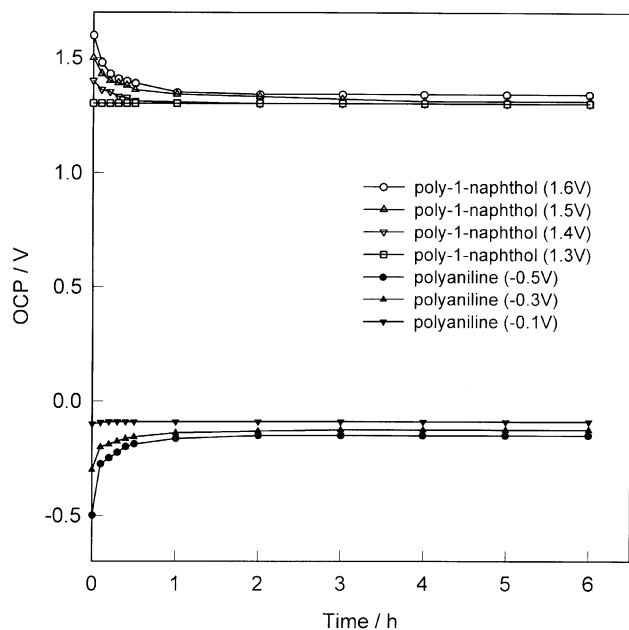
Anode Material: Polyaniline

Reduced (insulating) form   Oxidized (conducting) form

Cathode Material: Poly-1-naphthol

Reduced (insulating) form   Oxidized (conducting) form

Fig. 2. The redox processes involved in the electroactivity of polyaniline (first step) and poly-1-naphthol.

Fig. 3. Open-circuit potential (OCP) of polyaniline and poly-1-naphthol versus time in 0.2 M LiClO$_4$ + 0.01 M HClO$_4$ in MeCN. The polymers were formed by 100 cycles and preconditioned at the specified potentials before monitoring OCP.

The life cycle of the cell capacity and the percentage of the coulombic efficiency (CE%), were tested by cyclic voltammetry. Capacity (the amount of the charge passed in the charging by oxidation or discharging by reduction) was estimated as a function of the cycle number and CE was calculated as the ratio of the discharging capacity to the charging capacity at one and the same cycle number (Fig. 4). The figure shows that the capacity deteriorate rapidly during the first 50 cycles and then stabilized, with 15 and 23% loss in capacity of discharging and charging, respectively, after 100 cycles. On the other hand, CE% improved with increasing the cycle number from 92% at the beginning to 99.6% after 100 cycles. The capacity loss is attributed to partial degradation of the polymers and leaching of some loosely attached polymer chain during the volume change on charging and discharging. After 1 week under the open-circuit conditions, the discharging/charging cycle showed ∼5% decrease in capacity due to the self-discharge.

Galvanostatic discharging and charging was used to evaluate the capacity, the energy and the power performance of the cell. According to Faraday's law and formulas given in Fig. 2, the theoretical full capacity of polyaniline and poly-1-naphthol are 298 and 171 Ah kg^{-1}, respectively. Fig. 5 shows the cell voltage versus capacity curves for the first discharging/charging cycle at 1.0 mA cm^{-2}. The specific capacity (Ah kg^{-1}) was estimated from the capacity (Ah)
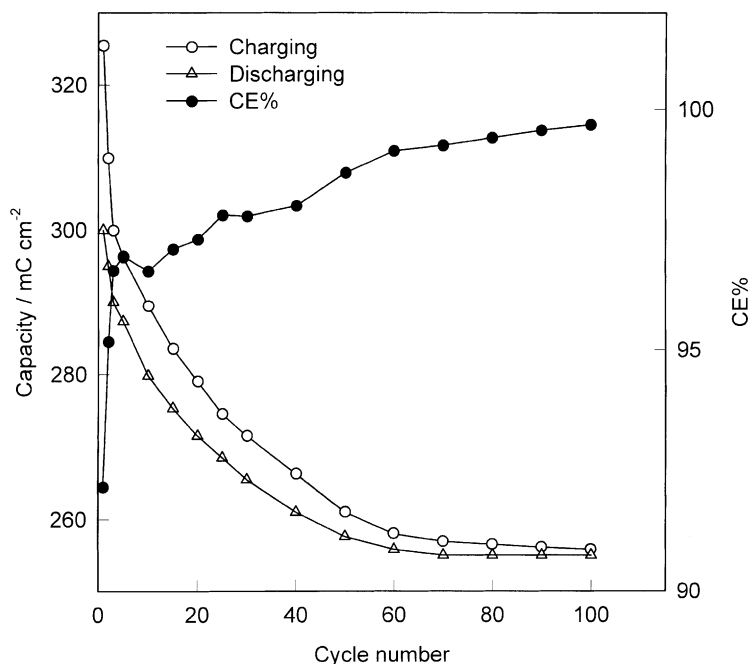
Fig. 4. Dependence of the cell capacity on the cycle number. The cell voltage was cycled from 0–1.4 V at a scan rate of 10 mV s^{-1}. Polyaniline = reference and counter electrodes and poly-1-naphthol = working electrode. The films were formed by 100 cycles.

divided by the mass of polyaniline + poly-1-naphthol layers on the electrodes (kg). The figure shows that the cell voltage decreases/increases gradually as the depth of the discharging/charging increases. From the figure, the cell specific capacity (down to an emf of 0.4 V) is 150 Ah kg^{-1} while the specific energy at a 1.0 V cutoff is 113 W h kg^{-1}. A zero-Ω
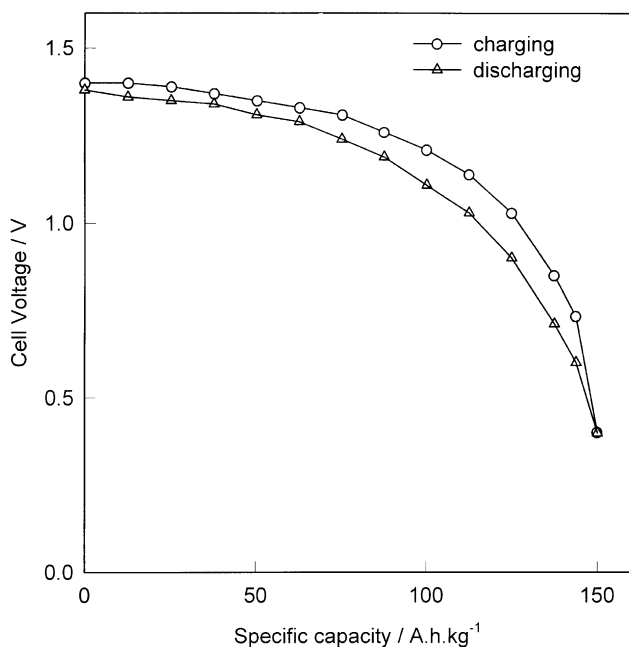

Fig. 5. Galvanostatic discharging/charging curves for the cell: polyaniline/ 0.2 M LiClO$_4$ + 0.01 M HClO$_4$ (MeCN)/poly-1-naphthol at 1.0 mA cm^{-2}. The films were formed by 100 cycles.

Ammeter indicated a current density of 12.8 mA cm^{-2} for the cell. This means that a maximum specific power of ∼9 kW kg^{-1}, at the OCP of the cell, or a power density of 180 W m^{-2} could be obtained from this cell. The high power density is attributed the extended surface area of the polymer layers compared to the conventional metal electrode. Repetitive galvanostatic charging/discharging at 1.0 mA cm^{-2} showed a gradual deterioration in the discharging capacity up to 21% loss in capacity after 100 charging/discharging cycles.

It should be mentioned that when the thicker layers formed by 600 cycles were used as the active materials in the cell, the OCP remains the same as shown in Fig. 3. However, the life cycle deteriorated much rapidly than with the 100-cycle layers and 65% loss in the capacity was observed after 10 galvanostatic charging/discharging cycles. This is attributed to the poor adhesion between the polymer layers and the electrode surface. Actually, during the charging/discharging processes parts of the polymer layers could be seen falling down from the electrode surface. Another reason is the large change in the layer dimensions (swelling and shrinking) on the insertion of the counter ions and the solvent molecules into the layer and their removal from the layer during the charging and discharging. The adhesion of the polymer layers should be improved to ensure good performance of the cell over a long life cycle.

In conclusion, a new rechargeable cell made of polyaniline and poly-1-naphthol as electrode materials and use LiClO$_4$ + HClO$_4$ in MeCN as electrolyte was characterized and showed some promising properties over the conventional metal cell.

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