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Short communication

Polyaniline nanofibres as a cathode material for rechargeable lithium-polymer cells assembled with gel polymer electrolyte

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Abstract

Polyaniline nanofibres of high conductivity were prepared by interfacial polymerization. The polyaniline nanofibres were used as an active cathode material in lithium-polymer cells. Gel polymer electrolyte (GPE) based on the porous poly(vinylidene-*co*-hexafluoropropylene) P(VdF-*co*-HFP), membrane was prepared and used as an electrolyte material in assembling Li/GPE/polyaniline cells. The electrochemical properties of the cells were investigated by cyclic voltammetry and charge–discharge cycling tests. The cell delivered a maximum discharge capacity of 69 mAh g^{-1} at 20th cycle and 48 mAh g^{-1} at 100th cycle with 97% coulombic efficiency.

Keywords: Conducting polymer; Lithium-polymer cell; Nanofibre; Polyaniline; Polymer electrolyte

1. Introduction

There is an increasing need for rechargeable batteries of high specific energy for portable electronic equipment, electric vehicles, and load-levelling systems. Hence, intense and diversified research work is being pursed on various electrode and electrolyte materials for developing such batteries. As cathode materials, conducting polymers are expected to deliver high specific capacity. The theoretical values of specific capacity of conducting polymers are comparable with those of metal oxide electrodes and the added advantages of the lower cost and easy synthesis of the polymers given them an edge over metal oxide cathodes for rechargeable lithium batteries [1]. Among the conducting polymers, polyaniline has been widely studied because of its high stability in air, and high conductivity, and because it satisfies most of the basic requirements of an electrode material for a light-weight battery [2–5]. The promising behaviour of polyaniline has resulted in its applicability to a level whereby it has been employed in commercial lithium cells manufactured by Seiko Electronic Components, Ltd.

In recent years, nano-structured polyaniline has been tested for sensor, actuator, supercapacitor and gas-separation membrane applications [6–11]. To the best of our knowledge, however, there has not been any investigation of the exclusive application of nano-structured polyaniline to rechargeable batteries. As a nano-structured conducting polymer has a higher electroactive surface area exposed to the electrolyte, both charge-transfer and mass-transport phenomena are expected to improve significantly. It is therefore expected that nano-structured polyaniline will perform better than its macroscopic counterpart in rechargeable batteries. Hence, in this study, polyaniline nanofibres are prepared by a interfacial polymerization technique and their electrochemical performance as a cathode material is evaluated in lithium-polymer batteries assembled with gel polymer electrolyte.

2. Experimental

Polyaniline nanofibres were synthesized by interfacial polymerization as reported in literature [8], which is briefly described as follows. A 0.3 M sample of aniline was dissolved in 500 ml of CH_2Cl_2. Ammonium persulfate (0.075 M) was dissolved in 1.0 l of water containing 1.0 M of $HClO_4$. This aqueous solution was carefully spread over the above organic solution of monomer

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and kept undisturbed at 25 °C for 24 h. The solution was filtered, and then washed with copious amounts of water and acetonitrile until the filtrate was colourless. Doping and de-doping of the polymer was achieved by stirring the polymer in 1.0 M $HClO_4$ and 0.2 M NH_4OH, respectively, for 15 h. Then, it was filtered and vacuum dried at 40 °C overnight. The morphological structure of the polyaniline nanofibre was examined using a scanning electron microscope (JEOL, JSM-6300).

To prepare the polymer cathode, polyaniline nanofibres (75 wt.%) were mixed in an aqueous medium with Super-P (18 wt.%) and vapour-grown carbon fibre (VGCF) (2 wt.%), which serves as a conducting material, and with carboxy methyl cellulose (CMC) (3 wt.%) and styrene-butadiene rubber (SBR) (2 wt.%) as a binder. The resulting mixture was ball milled for 15 h and then the slurry was cast on an aluminium foil to a thickness of 70 μm by means of a doctor blade. The electrode was dried in a vacuum oven and then roll pressed to enhance particulate contact and adhesion to the foil. The thickness of the electrode after roll pressing was about 30 μm. The anode consisted of a lithium foil of 50-μm thickness (Cyprus Foote Mineral Co.) that was pressed on to a copper current-collector.

A gel polymer electrolyte (GPE) based on a porous P(VdF-*co*-HFP) membrane was prepared as follows. P(VdF-*co*-HFP) (Kynar, 2801), fumed silica, dibutyl phathalate (DBP) and acetone were mixed together and ball milled for 48 h and then cast on a glass plate using a doctor blade. After 30 min, the membranes were immersed in methanol to remove the DBP. The membranes were then vacuum dried at 60 °C for 12 h. When using the membrane in the cell assembly, it was gelled by immersing in 1.0 M $LiClO_4$ dissolved in ethylene carbonate (EC)/propylene carbonate (PC) (1:1 by volume) for 1 h.

Cyclic voltammetry was performed on a polyaniline working electrode, with counter and reference electrodes of lithium, at a scan rate of 0.5 mV s^{-1}. The Li/GPE/polyaniline cells were assembled by sandwiching the GPE between a lithium anode and a polyaniline cathode. The cells were enclosed in a metallized plastic bag and vacuum-sealed. All cell assemblies were carried out in a dry-box that was filled with argon gas. Charge and discharge cycling tests of the Li/GPE/polyaniline cells were conducted over a voltage range of 2.0 to 3.9 V with a Toyo battery-test equipment (TOSCAT-3000U).

3. Results and discussion

Several techniques, which include electrospinning [12] and template-assisted chemical and electrochemical methods [13–16], have been adopted in preparing nano-structured polyaniline. In order to prepare a bulk quantity of the material for practical applications, the chemical route that requires less stringent experimental conditions is preferable. Hence, we applied an interfacial polymerization technique [8] to produce a bulk quantity of the polyaniline nanofibres as a cathode active material. Scanning electron microscopic (SEM) analysis of the polyaniline prepared by this route revealed a nanofibrous structure of fibres with diameters of ∼90 nm and lengths of ∼420 nm (Fig. 1). Upon de-doping the nanofibres, the diameter is found to be slightly increased, as is the case with the conventional polyaniline. The electrical conductivity of the polyaniline nanofibres was found to be 1.0 S cm^{-1} by means of the four-probe method. This is twice the reported value of 0.5 S cm^{-1} [8]. The conductivity of the as-synthesized polyaniline nanofibres, which were washed only with water and 1.0 M $HClO_4$, is 0.1 S cm^{-1}. By contrast, the same material after washing with copious amounts of acetonitrile, until the filtrate was colourless, is 1.0 S cm^{-1}. This result clearly shows that the low molecular weight fractions of polyaniline are removed by washing with acetonitrile, and thereby give rise to an improvement in the conductivity of the polymer.

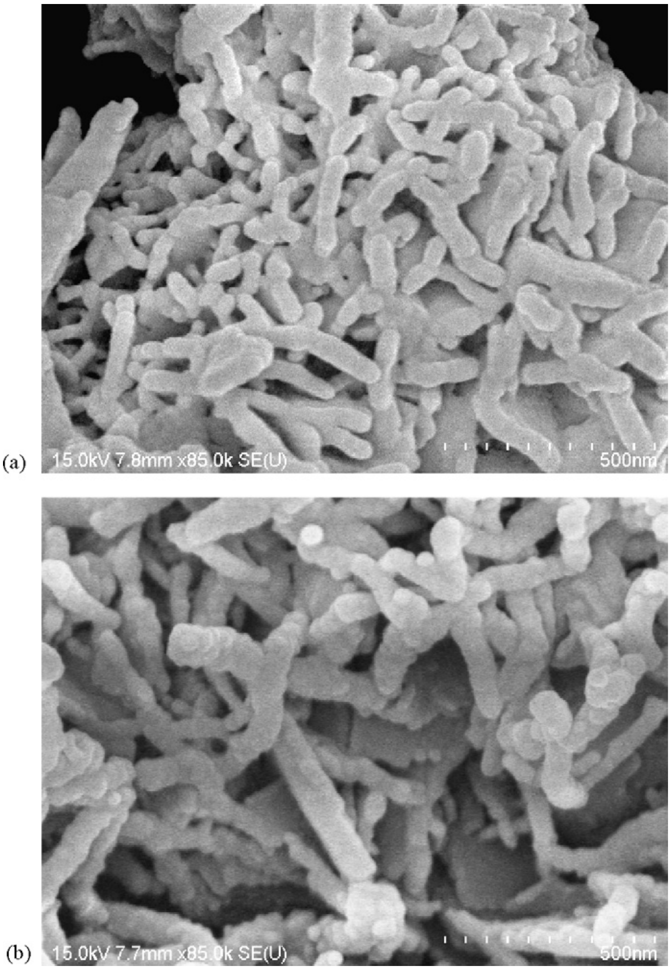

Fig. 1. Scanning electron micrographs of polyaniline nanofibres: (a) doped form and (b) de-doped form.

A typical SEM image of a porous membrane prepared with P(VdF-*co*-HFP) and SiO_2 by solvent extraction is presented in Fig. 2. The SiO_2 spherical nanoparticles are well-distributed in the membrane. The addition of fumed silica increases the capability to hold liquid electrolyte and to reinforce the physical strength of the membrane, as previously reported [17]. The membrane has a porous structure, which reflects a high exchange rate between DBP and methanol during immersion precipitation. The microporous structure of the membrane can lead to efficient uptake of the liquid electrolyte when it is soaked in an electrolyte solution, and this finally results in gelation of the membrane. The

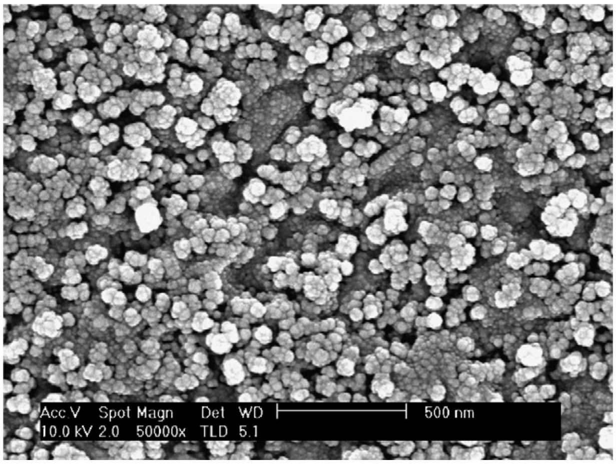

Fig. 2. Scanning electron micrographs of the porous membrane prepared with P(VdF-*co*-HFP) and SiO_2.

thickness of the porous membranes is about 50 μm. The membrane was immersed in electrolyte solution (1.0 M $LiClO_4$ in EC/PC) for 1 h before cell assembly. The ionic conductivity of the gelled membrane is 1.5×10^{-3} S cm^{-1} at room temperature. The uptake of liquid electrolyte is measured to be 133% of the weight of the porous polymer membrane. Linear sweep voltammetry of the GPE shows the onset of an oxidation current above 5.0 V versus Li, which can be assigned to the decomposition voltage of the GPE. Hence, this GPE is found to be suitable for operation in a potential window of 2.0–3.9 V, which is employed in the present study.

Cyclic voltammograms of the polyaniline electrode are given in Fig. 3. The positive currents are for oxidation and the negative currents are for reduction. A broad oxidation peak (doping of anion into the polymer) between 3.0 and 3.4 V and a reduction peak (de-doping of anion from the polymer) at 2.9 V are observed. Upon successive cycles, both the oxidation and the reduction peak currents are found to increase continuously. This indicates a slow and continuous penetration of the electrolyte into the inner layers of the polyaniline electrode. This results in a continuous increase of available polymer material for the redox process. The reversible behaviour of the redox peaks confirms the reversibility of the doping and de-doping process of the polyaniline electrode upon cycling.

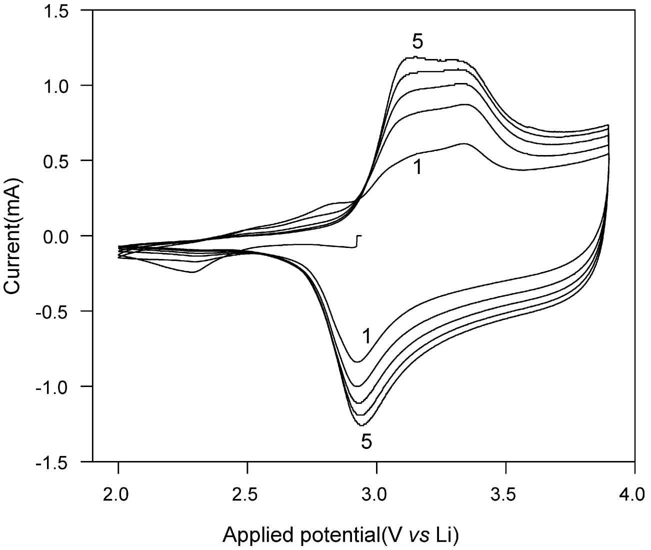

Fig. 3. Cyclic voltammograms of polyaniline electrode at a scan rate of 0.5 mV s^{-1}. Numbers represent the cycle number.

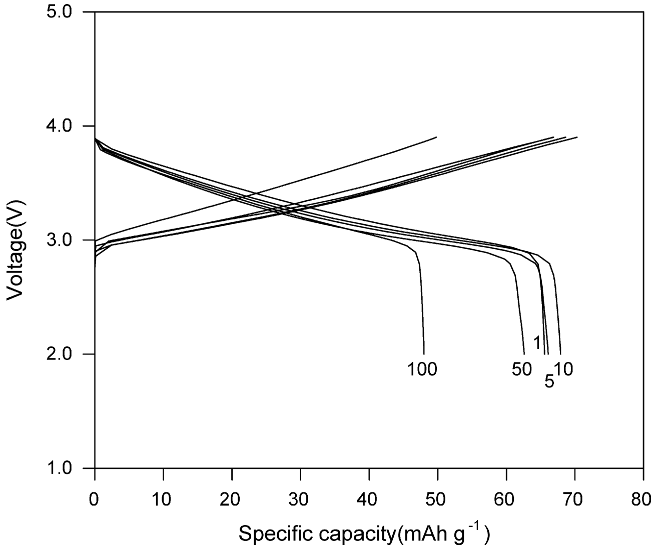

Fig. 4. Charge–discharge curves of the Li/GPE/polyaniline cell at a current rate of 0.2 C. Numbers represent the cycle number.

The charge–discharge profiles of randomly selected cycles of a Li/GPE/polyaniline cell, which are measured at a constant current density of 0.059 mA cm^{-2} (0.2*C* rate), are shown in Fig. 4. It should be noted that the cycling tests are performed without applying external pressure to the cell. The cell displays typical charge–discharge curves and the voltage drop in passing from charge to discharge is relatively small, which means that the cell has a low resistance. A specific discharge capacity of 63 mAh g^{-1} based on polyaniline nanofibres is obtained on the first cycle. The cell shows the steep discharge between 2.8 and 2.0 V, which suggests that operating voltages of these cells may be taken approximately to be above 2.8 V.

Plot of discharge capacities and coulombic efficiency as a function of cycle number are given in Fig. 5. Up to 20 cycles, the discharge capacity is found to increase slowly and deliver a maximum of 69 mAh g^{-1} at 20th cycle. This behaviour is in accordance with the cyclic voltammograms that show continuously increasing redox peak currents with successive cycles. After about 20 cycles, the capacity starts to fade smoothly and becomes 48 mAh g^{-1} at the 100th cycle. This feature is presumed to be mainly due to the instability of the polyaniline electrode. As demonstrated by the SEM data in Fig. 1, polyaniline nanofibres undergo shrinkage and swelling during charging (doping of anion) and discharging (de-doping of anion) processes, respectively. This volume change may lead to degradation of the electrode contact during cycling. The coulombic efficiency of the cell is calculated to be around 95% for the initial 20-cycles period (Fig. 5) and slowly increases to attain a value of 97% at the 100th cycle.

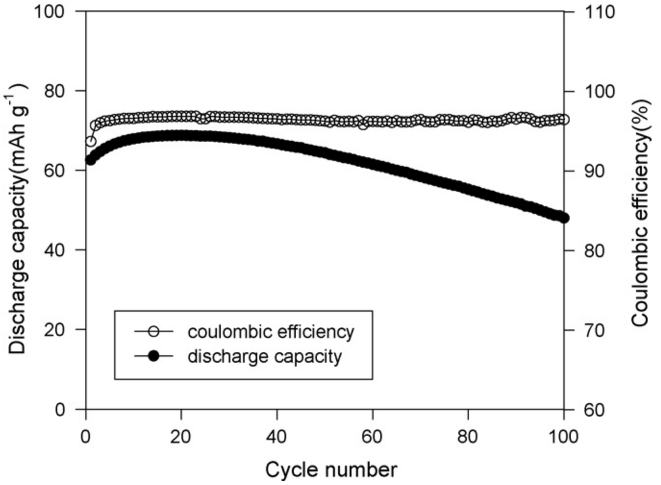

Fig. 5. Discharge capacity and coulombic efficiency of Li/GPE/polyaniline cell as function of cycle number. Cycling conducted at 0.2*C* rate between 2.0 and 3.9 V.

The specific capacity and coulombic efficiency values of the present study are much higher than those of the solid-state polyaniline cells reported by Changzhi et al. [18]. They reported that a Li/polyaniline cell using a polymer electrolyte of PEO-epoxy resin-$LiClO_4$, delivered a specific capacity of 18 mAh g^{-1}, with 90% coulombic efficiency. The cell was operated between 2.0 and 4.0 V at a constant current of 50 μA applied to an electrode area of 1.4 cm^2. Thus, it is seen that the performance of a lithium cell made with polyaniline nanofibres as a cathode together with a GPE is much better than that of a cell made with poly(ethylene oxide)(PEO)-based polymer electrolyte. It is presumed that the higher specific capacity of the former is due both to the nano-structure of the polyaniline, which facilitates access of the electrolyte, and the GPE, which has a higher ionic conductivity at room temperature. The rate capability of the Li/GPE/polyaniline cell is shown in Fig. 6. The voltage profiles remain almost unchanged on increasing the current rate from 0.1 to 2.0 C, with a gradual decrease in discharge capacity. At a current rate of 2.0 C, the cell gave a specific capacity of 49 mAh g^{-1}, which corresponds to 67% of the capacity obtained at the 0.1*C* rate.

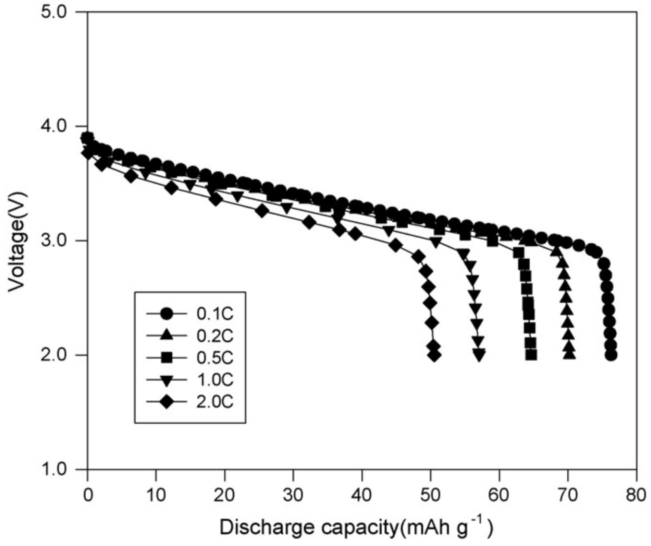

Fig. 6. Discharge profiles of Li/GPE/polyaniline cell at different current rates.

In order to improve the cycle-life of the Li/GPE/polyaniline cells, it is considered that the polyaniline should be mechanically supported to suppress shrinkage and swelling during cycling. To achieve this, polyaniline can be made as composite by coating on the carbon nanotubes, and thereby the mechanical strength of the polymer can be increased concurrently by exploiting the advantage of the nano-structured electro-active material. Further evaluation of a polyaniline-coated carbon nanotube composite as a cathode active material in rechargeable lithium-polymer batteries is underway in our laboratory.

4. Conclusions

Polyaniline nanofibres have been synthesized by interfacial polymerization and this material is employed as a cathode material in rechargeable lithium-polymer cells together with gel polymer electrolyte. The cell delivers a maximum specific capacity of 69 mAh g^{-1} at 20th cycle and 48 mAh g^{-1} at 100th cycle, with 97% coulombic efficiency. The higher value of specific capacity compared with that of a PEO-based polyaniline cell is considered to be both due to the nano-structure of the polyaniline, which facilitates the easy access of the electrolyte, and to the GPE, which has higher ionic conductivity at room temperature. A decrease in discharge capacity with cycling is presumed to be the effect of volume change in the polyaniline nanofibres, which leads to degradation of the positive electrode. This degradation effect of the nanofibrous-polyaniline electrode can be overcome by using the composite of polyaniline with carbon nanotubes.

Acknowledgments

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