

Preparation of polyaniline-poly (*p*-styrenesulfonic acid) composite by post-polymerization and application as positive active material for a rechargeable lithium battery

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Polyaniline (PANI)-poly (*p*-styrenesulfonic acid) (PSS) composite was prepared by thermal post-polymerization of PANI-*p*-styrenesulfonic acid (SSA) composite. A PANI-SSA composite was prepared by mixing PANI/*N*-methyl-2-pyrrolidinone solution with SSA aqueous solution. The PANI-SSA composite film was prepared by casting the composite onto an ITO glass plate. The cast film was converted to PANI-PSS film by heating at 100 °C for 3 h (post-polymerization process). The PANI-PSS modified ITO electrode showed electrochemical responses based on the redox reaction of PANI-PSS composite in the organic electrolyte solution, for example, propylene carbonate containing 1 mol dm⁻³ LiClO₄. The PANI-PSS composite was a cation-doping polymer composite. The composite was also modified on a porous carbon material (Reticulated Vitreous CarbonTM, RVC, Energy Research and Generation, Inc.). The PANI-PSS modified RVC electrode showed similar electrochemical behaviour as the PANI-PSS modified ITO electrode. Model secondary lithium cells, Li|1 mol dm⁻³ LiClO₄-propylene carbonate|PANI-PSS modified RVC electrode, were constructed and charge-discharge cycling tests were carried out. The cell showed about 60% coulombic efficiency under high current density cycling conditions (3.8 A g⁻¹, per gram of PANI-PSS modified RVC electrode).

1. Introduction

Polyaniline (PANI) is one of the most promising materials for electrochemical devices, such as light-weight batteries [1, 2], capacitors [3], and electrochromic devices [4, 5]. PANI is stable in air and has high conductivity at ambient temperature. However, the low solubility of PANI to general solvents limits its advanced application to other devices. Recently, by changing the counter ions (dopant anions) PANI has been soluble in common solvents. For example, Cao *et al.* [6] reported a method for inducing solubility of PANI by substituting the originally incorporated counter ions (dopant anions, e.g. ClO₄⁻, Cl⁻, SO₄²⁻) for other anions such as 4-dodecylbenzenesulfonate ion. Tzou and Gregory [7] also reported the preparation of soluble PANI using various organic acids. Furthermore, MacDiarmid *et al.* [8] discovered the concept of secondary doping of PANI by using such soluble PANI.

We have applied the organic molecule doping technique to functionalize PANI and create a new type of PANI derivative. We selected *p*-styrenesulfonic acid (SSA) as a dopant anion for PANI. SSA

has a double bond as a reactive site (polymerization or addition site) and a sulfonic acid moiety for doping PANI. We have applied PANI-*p*-styrenesulfonic acid (SSA) composite to a Schottky diode [9, 10]. The electrochemical preparation of the PANI-SSA composite and its post-polymerization was also reported [11].

In this paper we report preparation of a soluble PANI-SSA composite and its application as a modifier for various substrates. The substrates for the PANI modified electrode is an ITO glass plate and Reticulated Vitreous CarbonTM (RVC). The ITO glass plate was a glass plate with a conducting coating of indium oxide-doped tin oxide on one side. RVC has many open pores, with a honeycomb structure, composed almost solely of vitreous carbon. Detailed properties of RVC material have been reported in the literature (e.g., [12]). After modification of the substrates with PANI-SSA composite they were heated to polymerize SSA molecules in the composite and the structure of post-polymerized PANI-SSA composite (PANI-PSS) was confirmed by Raman spectroscopy. The electrochemical behaviour of PANI-PSS composite in the organic electrolyte solution and charge-discharge cycleability of model cells (Li/PANI-PSS modified RVC electrode) were also investigated.

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2. Experimental details

2.1. Materials

All chemical reagents were purchased and used without further purification. Polyaniline (PANI) was prepared by oxidation of aniline with ammonium persulfate [7]. The PANI powder was converted to PANI base form by treatment with 3.0% ammonium hydroxide aqueous solution. Reticulated Vitreous CarbonTM (RVC, Energy Research and Generation Co.) was a gift from Tomoe-Kogyo Co. (Japan). The porosity grade of the RVC was 100 pores per inch.

2.2. Preparation of polyaniline-*p*-styrenesulfonic acid composite

Typical preparation of polyaniline-*p*-styrenesulfonic acid composite (PANI-SSA) was as follows. Polyaniline powder (1.0 g) was dissolved in 100 ml of *N*-methyl-2-pyrrolidinone and some of the insoluble material in the solution was filtered off. *p*-Styrenesulfonic acid aqueous solution was prepared by passing sodium *p*-styrenesulfonate aqueous solution (0.5 g/30 ml) with the cation exchange resin (DiaionTM SK1B, Mitsubishi Chemical). The SSA aqueous solution was added to the PANI/*N*-methyl-2-pyrrolidinone solution under cooling with an ice bath and the mixture was permitted to stand for 24 h at room temperature (20–25 °C). The precipitate was collected by centrifugation, stored in the solvent, and used as was, since insoluble mass was produced by removing solvent.

2.3. Preparation of PANI-PSS modified electrode

The PANI-PSS modified ITO electrode was prepared by casting the PANI-SSA composite onto a ITO glass plate (area 1 cm²), removing the solvent, and heating for 3 h at 100 °C. The PANI-PSS modified RVC electrode was prepared by dipping a RVC electrode (0.5 cm × 0.5 cm × 2 cm, 77 mg) into the PANI-SSA composite/solvent mixture and heating for 5 h at 100 °C. The amount of loaded PANI-PSS composite on this size of RVC electrode was typically 1 mg.

2.4. Electrochemical measurements

Cyclic voltammetry was carried out using a conventional three-electrode cell. The reference electrode was a lithium tip electrode in organic electrolyte solution such as propylene carbonate. Potential is cited against the Li/Li⁺ reference electrode unless otherwise mentioned. The counter electrode was a lithium foil or platinum plate. The working electrode was PANI-PSS modified ITO electrode or PANI-PSS modified RVC electrode. Voltammograms were recorded with a potentiogalvanostat (HA-301, Hokuto), function generator (HB-104, Hokuto), and X-Y recorder (WX-1100, Graphtec). Charge-discharge cycling tests

of model cells were performed with a charge-discharge controller (NCD-1S, Nikko Keisoku).

2.5. Measurements

Infrared spectra of PANI composites were measured using a FTIR-4200 spectrophotometer (Shimadzu). Raman spectra of PANI-SSA and PANI-PSS composite films were collected with a JASCO NR-1800 Raman spectrophotometer. The excitation line was an argon laser at 514.5 nm. Scanning electron microscopic photographs of PANI-PSS modified electrodes were taken with a Hitachi S-2300 scanning electron microscope. The conductivity of PANI-PSS composite was measured using a two-electrode cell with an a.c. impedance measurement system (HZ-1AC, Hokuto).

3. Results and discussion

3.1. Characterization of polyaniline-*p*-styrenesulfonic acid composite and polyaniline-poly (*p*-styrenesulfonic acid) composite

To confirm whether *p*-styrenesulfonate molecules in the PANI-SSA composite can be polymerized by heating at 100 °C for 3 h as a post-polymerization process, Raman spectra of the PANI-SSA and heat treated PANI-SSA composite were measured. Figure 1 shows the spectra (from 1700 cm⁻¹ to 1500 cm⁻¹) of the PANI-SSA film (a) and heat treated PANI-SSA film (b).

The PANI-SSA film shows a broad peak around 1590 cm⁻¹. The broad peak was due to the overlapping PANI band (about 1590 cm⁻¹) and double bond stretching band (about 1610 cm⁻¹) in SSA. After the heat treatment the spectrum changed as shown in Fig. 1(b). The peak intensity at 1610 cm⁻¹

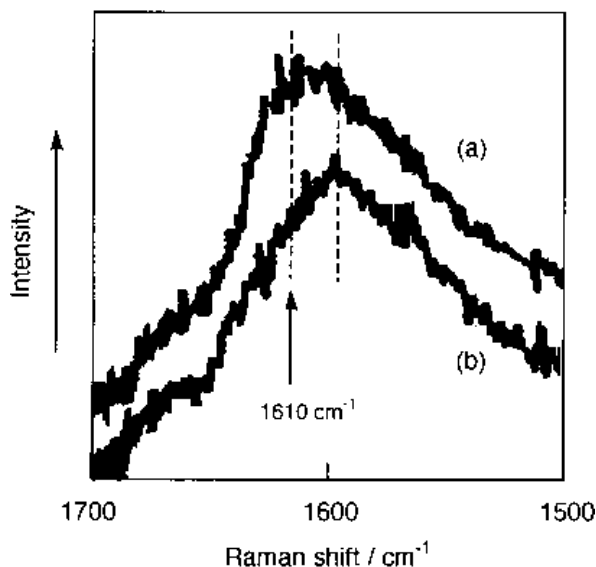


Fig. 1. Raman spectra of PANI-SSA composite film (a) and heat treated PANI-SSA composite film (for 3 h at 100 °C). Excitation at 514.5 nm (Ar laser).

decreased. The peak in Fig. 1(a) shifted slightly to a lower wavenumber. This suggests that a decrease in the number of double bonds in the composite film. Thus PANI-SSA composite film was partially post-polymerized by the heat treatment. However, some double bonds remained in the heated PANI-SSA film. Hereafter, the heated PANI-SSA composite film is indicated as PANI-PSS film. The conductivity of PANI-PSS film was $3.1 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C.

Figure 2 shows SEM photographs of PANI-PSS modified ITO electrode, RVC electrode, and PANI-PSS modified RVC electrode.

The surface of the PANI-PSS modified ITO electrode is smooth and homogeneous. Usually, PANI surfaces prepared by electrochemical oxidation have a globular structure (e.g., [13]). Such a smooth surface structure suggests that the PANI and PSS

polymer chains were mixed homogeneously and in a densely packed form in the film.

The RVC electrode has a honeycomb-like carbon flame as shown in Fig. 2(b). The PANI-PSS composite was modified in the carbon flame (Fig. 2(c)). The modified PANI-PSS composite has a globular structure. The structure is produced by a combination of the hydrophobicity of the RVC surface and hydrophilicity of the PANI-SSA composite. Such small globular structures enlarge the electrochemically active surface area of the composite.

3.2. Electrochemical behaviour of polyaniline-poly(*p*-styrenesulfonic acid) composite in organic electrolytes

Electrochemical responses of a PANI-PSS film prepared by post-polymerization of PANI-SSA were investigated in organic electrolyte solutions such as propylene carbonate to confirm the applicability of the composite as a positive material in lithium batteries. Figure 3 shows the cyclic voltammograms for a PANI-PSS modified ITO electrode in 1.0 mol dm^{-3} LiClO_4 /propylene carbonate solution.

Two anodic peaks at 3.08 V and 3.88 V and two cathodic peaks at 3.02 V and 3.70 V were observed. This suggests that the PANI-PSS composite film is electrochemically active in the organic solution. The peak separation between the corresponding anodic and cathodic peaks was 0.06 V (1st peak pair) and 0.18 V (2nd peak pair). This indicates that the redox reaction in the polymer composite is reversible and active. The appearance of two such pairs of peaks

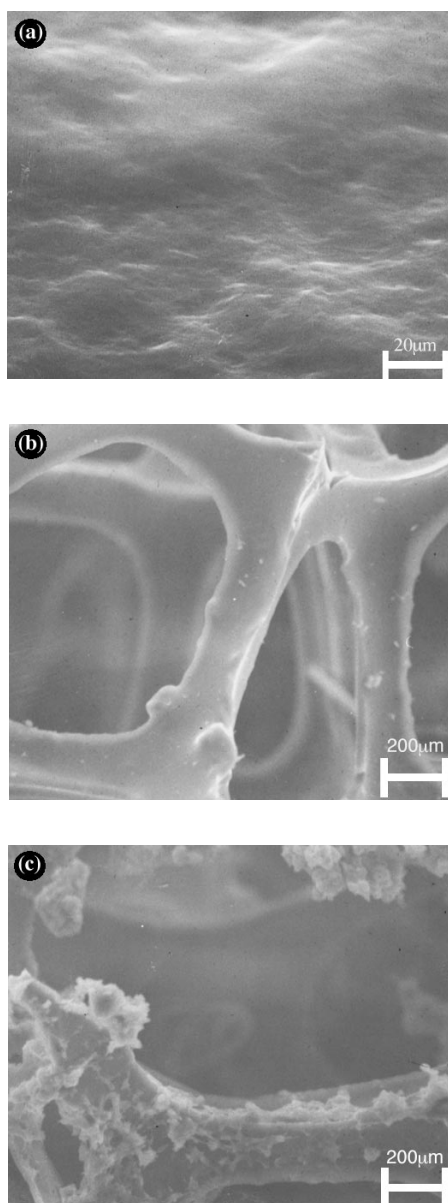


Fig. 2. SEM photographs of PANI-PSS modified ITO electrode (a), RVC electrode (b), and PANI-PSS modified RVC electrode (c).

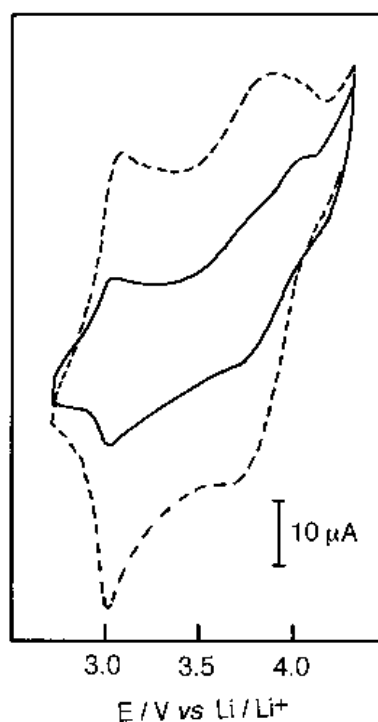


Fig. 3. Cyclic voltammograms for PANI-PSS modified ITO electrode in propylene carbonate solution containing 1 mol dm^{-3} LiClO_4 , solid line is 1st response and broken line is the response after 15 cycle between 2.7 V and 4.3 V. Scan rate: 10 mV s^{-1} .

also suggests that the electrochemical responses of PANI-PSS composite are similar to that of PANI prepared by electrochemical method in organic electrolyte [11]. The peak current increased with continuous potential scanning. This may be explained by the increase in the amount of electroactive PANI-PSS composite on the electrode. The surface of the PANI-PSS film on the electrode is densely packed by PANI and PSS chains as shown in Fig. 2(a). However, such a densely packing state is relaxed and the electrolyte solution penetrates the composite film with continuous potential scanning.

3.3. Cation doping of polyaniline-poly(*p*-styrenesulfonic acid) composite in organic electrolyte

The presence of dopant ion in PANI-PSS composite films was confirmed by cyclic voltammetry in organic solutions containing large anions such as laurylsulfonate. The usual PANI films, for example, PANI doped with ClO_4^- anion (PANI- ClO_4^-) did not show any electrochemical responses in the electrolyte solution containing large anions [11], because the large anions can not be doped into the PANI film and the electrochemical responses is absent. If a PANI composite film becomes a cation doping type film, the redox responses based on cation doping and dedoping processes are observed in the electrolyte solution containing such large size anions. Figure 4 shows the cyclic voltammogram for a PANI-PSS modified ITO electrode in propylene carbonate /1, 2-dimethoxyethane (1:1, by vol.) solution containing saturated sodium laurylsulfonate.

An anodic peak at 3.18 V and a cathodic peak at 3.05 V were observed. The potentials were almost the same as those of PANI-PSS composite in propylene carbonate containing $1 \text{ mol dm}^{-3} \text{ LiClO}_4$ (see Fig. 3). This suggests that sodium ions were doped from the electrolyte solution into the PANI-PSS composite

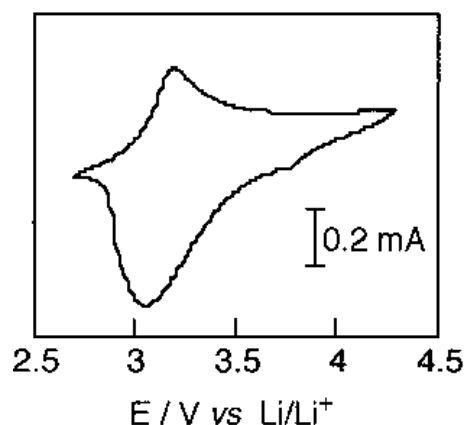


Fig. 4. Cyclic voltammograms for PANI-PSS modified ITO electrode in propylene carbonate/1,2-dimethoxyethane mixed solution (1:1, by volume) saturated with sodium laurylsulfonate.

film and dedoped from the film into the electrolyte. However, the second peaks were not observed. This may be due to the electrolyte containing a low concentration of sodium ion because of the low solubility of sodium laurylsulfonate. Cation doped polymer material is useful for a positive active material of rechargeable batteries because the battery can be operated with a small amount of electrolyte solution, that is, high energy density battery can be constructed. Therefore, PANI-PSS composite is promising for use in a rechargeable battery system as a positive material.

3.4. Charge-discharge behaviour of Li/polyaniline-poly(*p*-styrenesulfonic acid) composite electrode cell

Figure 5 shows charge-discharge curves of a Li/ $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$ -propylene carbonate/PANI-PSS modified RVC cell. The modified electrode for the model cell was used after its cyclic response became constant. The charge-discharge current density was 3.8 A g^{-1} (per gram of PANI-PSS modified RVC

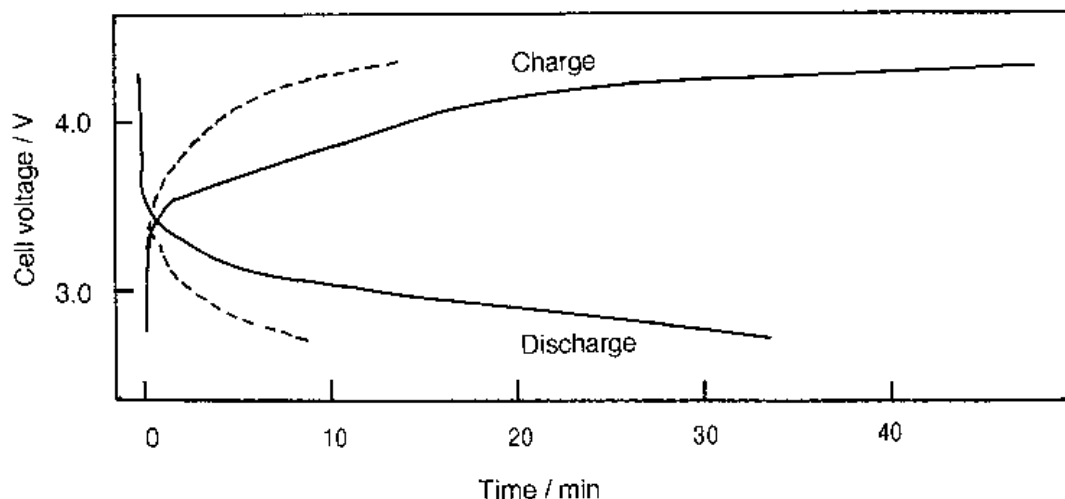


Fig. 5. Charge-discharge curves of Li/PANI-PSS modified RVC electrode cell. Current density 3.8 A g^{-1} (per gram of PANI-PSS modified RVC). Cycling between 2.7 V and 4.3 V. Electrolyte $1 \text{ mol dm}^{-3} \text{ LiClO}_4$ / propylene carbonate solution. Key: (—) 1st cycle, (---) 30th cycle.

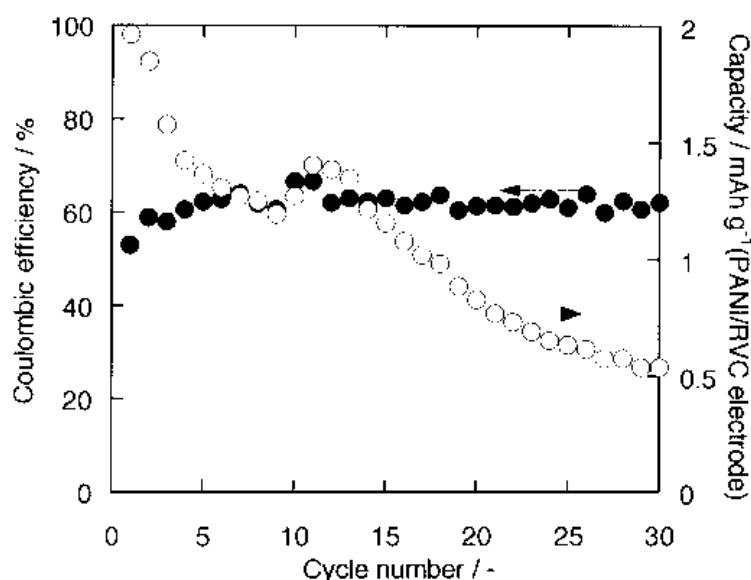


Fig. 6. Variation of coulombic efficiency (●) and discharge capacity (○) of Li/PANI–PSS modified RVC electrode cell with charge–discharge. Charge/discharge current density 3.8 A g^{-1} (per gram of PANI–PSS modified RVC). Cycling between 2.7 V and 4.3 V. Electrolyte $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{propylene carbonate}$ solution.

electrode). Charge and discharge cycling were performed between 2.7 V and 4.3 V. The potential decreased rapidly initially (about 1 min) in the discharge cycle. The potential decreased gradually from 3.2 V to 2.7 V (cutoff voltage). The first discharge capacity of the Li/PANI–PSS modified RVC electrode cell was 1.96 mA h g^{-1} (per gram of PANI–PSS modified RVC electrode). (The weight of modified PANI–PSS composite on the RVC electrode was 1 mg.) The discharge capacity of the Li/nonmodified RVC electrode cell was 0.53 mA h g^{-1} (per gram of RVC electrode). Thus, the net discharge capacity of first cycle based on the modified PANI–PSS composite was $112.5 \text{ A h kg}^{-1}$ (per kilogram of PANI–PSS composite). The energy density was $337.5 \text{ W h kg}^{-1}$ (per kilogram of PANI–PSS composite), based on the value of average voltage, 3 V. The large capacity of the Li/PANI–PSS modified RVC electrode cell is due to the large surface area of globular electrochemically-active PANI–PSS composite on the RVC electrode.

Figure 6 shows the variation of coulombic efficiency and capacity of the model cell with number of charge–discharge cycles. The coulombic efficiency of the cell was about 60% and the value was constant over 30 cycles. The capacity of the model cell gradually decreased with continuous cycling. After the

continuous charge–discharge cycling, the PANI–PSS composite peeled from the RVC electrode. Therefore, the capacity of the model cell decreased under high current density conditions. Optimization of the current density and the amount of modified PANI–PSS composite on the RVC electrode is indispensable to further application of PANI–PSS composites to a rechargeable lithium battery.

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