Two-step polyaniline loading in polyelectrolyte complex membranes for improved pseudo-capacitor electrodes

Abstract: A two-step polyaniline (PANI) loading procedure has been developed to produce polyelectrolyte complex composite membranes (CPECs) to be used as supercapacitor electrodes. In the first step, CPECs were prepared by co-precipitation of poly(styrene sulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC) mixed with various amounts of PANI as a filler. CPECs were formed by compression molding into 100 micron membranes using NaCl as a plasticizer and characterized for their electrochemical properties. In the second step, the highest capacitance CPEC membranes with 60% PANI loading were further modified and doped by crossflow polymerization of aniline through the composite membranes. By using a two-compartment crossflow reactor containing aniline and ammonium persulfate on each side, the PANI content of the composite membrane was further increased. Cyclic voltammetry showed a doubling in the capacitance of the membranes after the crossflow polymerization. The resulting electrodes were flexible with high capacitance and could be used to improve pseudocapacitor performance.

Keywords: polyaniline, supercapacitor, flexible electrode, polyelectrolyte complex, crossflow polymerization

1 Introduction

Much effort has been devoted to the development of supercapacitors (SCs) as lightweight and flexible energy storage with the main requirements being fast charge-discharge rate, high power density, and lower maintenance when compared to rechargeable batteries (1,2). Unlike traditional electrical double-layer capacitor (EDLC), pseudocapacitors accumulate energy through faradic reactions and display high specific capacitances, while maintaining high electrochemical performance (2–4). Electroactive materials used in the fabrication of such electrodes are typically based on polymers or metal oxides, which can store energy through redox reactions. Polyaniline (PANI) has been extensively studied for these applications as an electrically conducting polymer because of its doped redox mechanism, environmental stability, and its facile synthesis (5). PANI has a very high theoretical specific capacitance around 2,000 F g⁻¹, but its final value is largely dependent on the PANI synthesis and the electrode fabrication method (6,7). The microstructure of the PANI layer is known to play a major role in the electron transfer process and solvent/electrolyte interaction with the electroactive membrane. PANI can be blended with other materials such as graphene oxide, metal oxides, and carbon nanotube to improve its conductivity, surface area, or flexibility (8). Doping is also a strategy used to improve the electrochemical properties of PANI, and recently, Song et al. (9) doped PANI with imidazolium-based ionic liquids via in situ chemical oxidation polymerization leading to improved specific capacitance when compared to chloroacetic acid or hydrochloric dopant. Ionic liquids have the advantage of higher thermo and chemical stability and most importantly have a broader electrochemical usage window. Nevertheless, a major drawback when using PANI is its brittleness, so it is often used as a coating or blended in polymeric matrices to improve its flexibility (10). Nowadays, thin, lightweight, and flexible electrodes have become essential for the development of flexible electronics applications.

Among all possible polymeric materials that can be used as electrode matrix, polyelectrolyte complex membranes (PECs) have surprisingly received little attention.
The oppositely charged water-soluble polyelectrolyte can form a complex when mixed in solution and produce an insoluble polymer matrix. Schlenoff et al. reported that PEC membranes have relatively high ion diffusion coefficient because of their high free volume leading to high ion mobility (11). The utilization of PEC as the matrix for PANI immobilization to be used as flexible electroactive membranes is described in this study. The PECs were formed through electrostatic interactions and polymer chain entanglements (12,13) during the co-precipitation of polycationic poly(diallyl dimethyl ammonium chloride) (PDADMAC) and polyanionic poly(styrene sulfonate) (PSS) in solution with various amount of prepolymerized PANI powder. The obtained PANI–composite polyelectrolyte complex membranes (CPECs) were then formed using compression molding. The performances of the pure PEC membranes, pure PANI, and CPECs were compared and characterized for their electrochemical properties using cyclic voltammetry (CV) and electrical impedance spectroscopy (EIS).

2 Chemicals and methods

2.1 Chemicals

For PANI synthesis, aniline (ANI) (99%) was purchased from Panreac, and ammonium peroxydisulfate (APS; 98%) was purchased from Alfa Aesar. PSS was purchased from ACROS Organics and PDADMAC solution (20 wt% in water and \(M_w 2,000,000–3,50,000\)) was purchased from Sigma-Aldrich. Sulfuric acid purchased from Ensure was used as the electrolyte. All chemicals were used without purification.

2.2 Preparation of PANI

PANI was synthesized by a rapid mixing reaction where 0.3 M of ANI, as the precursor, was dissolved in 0.1 M \(\text{H}_2\text{SO}_4\). While maintaining vigorous stirring at room temperature, 0.3 M APS, as the oxidizing agent, was dissolved in 0.1 M \(\text{H}_2\text{SO}_4\) and then rapidly poured into the ANI solution. Polymerization of ANI started a few minutes later, and the color turned to green. The polymerization was carried out at room temperature and left undisturbed overnight. PANI was collected by filtration and was washed with deionized water repetitively until the filtrate became colorless. PANI solid residues were then dried at 70°C overnight and followed by grinding PANI to obtain fine powder. PANI powder has been pressed into thin pellets using hydraulic press with desired weight. The pressure used for the compression was 10 tons and held for 2 min at room temperature.

2.3 Fabrication of the PECs and CPEC

PECs were prepared by mixing 20 mL solutions of 0.1 M PSS and 0.1 M PDADMAC with 2 M NaCl. Herein, synthesized PANI was added to form CPEC with an increasing PANI content from 0% to 60% by weight. The CPECs were collected in the form of a precipitate and then compressed at 90°C for 10 min by using compression molding press at 2,000 psi. The obtained membranes were left to dry at room temperature and were cut into the appropriate size to be used as an electrode for electrochemical characterization.

3 Results and discussion

Schlenoff coined the term “saloplastic” to describe the plasticizing effect of the added salt in the PEC, which allows the polymer motion by screening the electrostatic interaction between oppositely charged polyelectrolytes (13). The salt left in PEC from the processing step can have an effect on the degree of hydration and water uptake, which also impacts the flexibility of the membranes. Yet the flexibility of the PANI composite PEC was found to decrease when the PANI weight fraction was increased above 60%, leading to brittle and unusable membranes. In Figure 1, the PEC membrane (Figure 1a) is shown as reference, while the flexibility of the composite CPEC (60% PANI) is shown in Figure 1b, which can withstand extensive deformation without cracking unlike pure PANI as shown in Figure 1c. The surface morphology of the PEC membranes and CPECs were characterized using SEM and shown in Figure 1d and e, respectively. The smooth surface of the PEC membranes is obtained from the interface of the Teflon sheet in the compression mold. In contrast, PANI aggregates can be seen on the SEM and reflect the much more viscous behavior of the CPEC.

Evidence of the increased brittleness of the composite membranes with the increasing PANI weight fraction content were provided by water uptake measurements. The plot of the calculated water uptake for membranes containing 0%, 20%, 40%, and 60% PANI is shown in
It can be clearly seen that the more hydrophobic PANI leads to a decrease in water uptake from 438%, which is commonly found for PEC, down to 172% which can still produce flexible membranes. The increase in the PANI weight fraction to 80 led to brittle and unusable membranes as discussed earlier.

FT-IR measurement in Figure 3 shows the spectra the initial PEC and the composite PEC–PANI membrane with pure ANI given as a reference peak. The C–H stretching at 2,930 cm$^{-1}$ corresponds to the PDADMAC found in the PEC membranes (a and c) as well as the broad peak at 3,400 cm$^{-1}$ of OH stretching from the moisture absorption. The lower moisture content and more hydrophobic nature of PANI can be seen here with almost no moist adsorbed. The absorption band at 1,290 cm$^{-1}$ is assigned to the C–N stretching of secondary aromatic amine, while the peak at 1,567 cm$^{-1}$ was ascribed to the nonsymmetrical C=C quinoid rings from the PANI structure. Peaks at about 1,033 and 1,076 cm$^{-1}$ in the fingerprint region correspond to the sulfonate group from PSS.

3.1 Effect of PANI weight %

It seems reasonable to hypothesize that the highest percent PANI loading in the CPEC would produce membranes having the highest capacitance. Surely from early results, as shown on Figure 1c, excessive PANI can lead to high brittleness. To find the optimum loading, PANI content was varied from 20% to 60% by weight, and the specific capacitance ($C_{sp}$) of the membranes was measured by CV. It is shown in Figure 4a that, as expected,
the $C_{sp}$ increased with the increasing PANI loading from 20% to 60%, where it reached a maximum of 31.7 F g$^{-1}$ with 40 mV s$^{-1}$ scan rate. Cycling performance (Figure 4b) was examined with CPEC with 60% PANI loading in 2 M sulfuric acid. The specific capacitance was calculated as retention percentage where the capacitance of the first cycle is 100%. After few cycles of the test, the capacitance of the system increased as ion penetration into the active site would take some time to be activated (17). The increase in capacitance during the first few cycles might ascribe to the full reaction of PANI (1,17–19). There was a slight decrease in the specific capacitance, and this might attribute to the swelling and the shrinkage during the faradaic reaction (20). This phenomenon might block the diffusion of ions into the membrane (21). However, the capacitance retention is stable up to 2,000 CV cycles.

3.2 Crossflow synthesis of PANI

It was demonstrated earlier that a 60% PANI loading in the PSS–PDADMAC complex membranes provided the best capacitance and by further increase of PANI loading...
would lead to too hydrophobic and too brittle membranes. Therefore, another strategy was used to further increase the loading of PANI in the membrane by in situ synthesis using a crossflow reactor. As shown in Figure 5, a two-compartment reactor was setup with the solution of ANI monomer on one side and the solution of APS on the other side. Preliminary data, not shown here, confirmed that the APS was able to cross the PEC. Nevertheless, during reaction, APS diffused across the membrane and reacted with the ANI monomer on the other side. As APS is an oxidant and an initiator for the oxidative polymerization of ANI into PANI, the PANI layer was produced at the surface of CPEC. This process resulted in the formation of an asymmetric membrane or Janus membranes. CPECs doped with crossflow PANI were further tested for their electrochemical activity and compared with the original CPEC with 60% PANI loading.

It is shown in Figure 6a that the specific capacitance of the electrode was increased after modifying the CPEC by the crossflow polymerization reaction and the CV area was increased by a factor of 1.8, and the increase in specific capacitance was measured at various scan rate from 1 to 50 mV s\(^{-1}\) as shown in Figure 6b. It is important to note that the changes in the mass of the electrode was insignificantly increased (less than 1%) and was negligible while the specific capacitance doubled. Such an increase can be rationalized by the fact that the electrochemical activity of PANI is more efficient at the surface of the electrode when compared to the bulk of the electrode. A recent review by Fleischmann et al. (22) has pointed out several strategies that induced the pseudocapacitive response, and one of them was to modify the interlayer to enhance ion transports, which is necessary for pseudocapacitive charge storage. In our experiment, measurements of the electrical conductivity of the original CPEC (composite membrane of 60% PANI) using a four-point probe setup revealed that the conductivity was \(5.72 \times 10^{-3} \pm 9.69 \times 10^{-4} \text{ S cm}^{-1}\) before crossflow polymerization. After the crossflow reaction, the electrical conductivity of the modified membrane was found to be \(7.11 \times 10^{-1} \pm 1.72 \times 10^{-1} \text{ S cm}^{-1}\) on the side facing the ANI solution and \(1.02 \times 10^{-2} \pm 3.46 \times 10^{-3} \text{ S cm}^{-1}\) on the side facing the APS.

4 Conclusions

In summary, composite membrane having PEC as the matrix and PANI as the filler was used to fabricate supercapacitor electrodes. Hence, the obtained \(C_{sp}\) of PANI and CPEC have similar values, while CPEC displayed excellent flexibility. Regarding the long-term usage of the electrodes, they were stable up to 2,000 cycles without any decrease in \(C_{sp}\). However, with further increase in the PANI content, the membranes were too brittle and were not practical for being used; therefore, the obtained CPECs were modified using the two-compartment crossflow diffusion to further in situ polymerize PANI. The \(C_{sp}\) of the modified CPEC increased up to 197% compared to the original CPEC. CPEC with PANI as the filler has high potential in the application of a novel, flexible, environmentally friendly, and high performance electrode.

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