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Carbon Papers with Conductive Polymer Coatings for Use in Solid-State Supercapacitors

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Summary: Conductive polymer-coated carbon papers have been fabricated through polymerisation of pyrrole-based monomers oxidised with various heteropolyacids. Smooth surfaces are obtained when multiple coatings are applied to the carbon surface and give good contact with the Nafion® electrolyte. Cyclic voltammetry was used to study the electrodes and a.c. impedance and charge / discharge cycling was used to study membrane electrode assemblies (MEA). MEAs were fabricated using a hot-press technique.

Keywords: conducting polymers; electrochemical capacitors; heteropolymetallates; polypyrroles; supercapacitors

Introduction

There is a requirement for more efficient and cleaner ways of producing energy and delivering power by replacing old technologies such as the Carnot-limited internal combustion engine. Viable alternatives include battery and fuel cells, which readily provide large amounts of energy for proposed automotive, portable and power utility applications. [1,2] The major disadvantage of these systems is low power capability caused by thermodynamic or electrode polarisation problems.[3] Supercapacitors (sometimes referred to as ultracapacitors or electrochemical capacitors) solve the power issue when placed in parallel. A hybrid system is high both in energy (a battery or fuel cell component) and in power (a supercapacitor component).[4] There are batteries, such as insertion lithium ion, which have improved power capabilities, but at the time of writing, these are expensive and suffer from temperature problems.

The supercapacitors under consideration in this study incorporate conductive polymer electrodes which store electrical charge faradaically in a three-dimensional system in a similar way to RuO_2-based systems.[5] Polymer electrodes previously studied for use within supercapacitors include polyaniline, polypyrrole and polythiophenes with various structures.[6,7]

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In this work polymer-coated carbon papers were chemically fabricated and tested as electrodes within a supercapacitor test cell. Polymer coatings were polypyrroles or poly(*N*-methylpyrrole)s doped with heteropolymetallates. The electrolyte is a Nafion® membrane, which was used to form a solid-state device with the coated electrodes. Nafion® could be considered as a safe alternative to corrosive aqueous acids or flammable and toxic organic-based electrolytes.

Single electrode fabrication and results

Carbon paper was pre-treated by washing in acetone and then hydrogen peroxide (30%) to remove grease and any other impurity. Multiple coatings of the polymer were grown chemically using aqueous heteropolyacids as oxidant solutions until full coverage of the carbon paper was obtained. The monomers, polypyrrole and *N*-methylpyrrole, were reacted separately with the heteropolyacids. (dodecamolybdophosphoric acid, dodecamolybdosilicic acid and dodecamolybdo-divanadophosphoric acid).

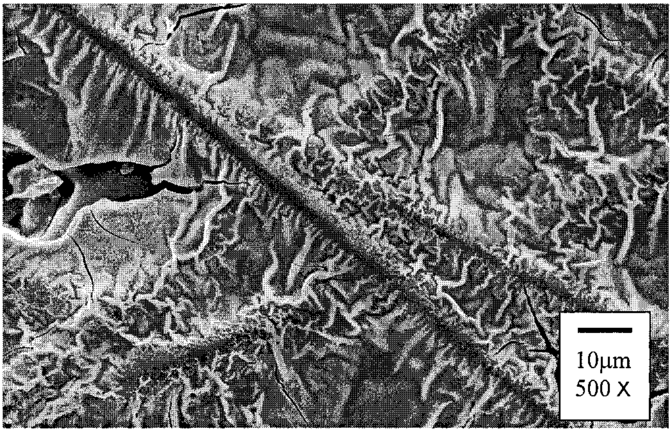

Figure 1. Scanning electron micrograph (secondary electron image) of carbon paper multiply coated with polypyrrole doped with dodecamolybdophosphoric acid.

Black conductive polymer coatings were obtained in both cases, which, when viewed using SEM (Figure 1), were all found to be smooth with a skin-like (pellicular) morphology. The wrinkled surface observed arises from the drying process in which the polymer coating contracts. The smooth surface is necessary for contact with Nafion® electrolyte, reducing any contact resistances that may occur. The polymer coatings adhered well to the surface of the carbon paper, having typical coating thickness 5 - 15 μm.

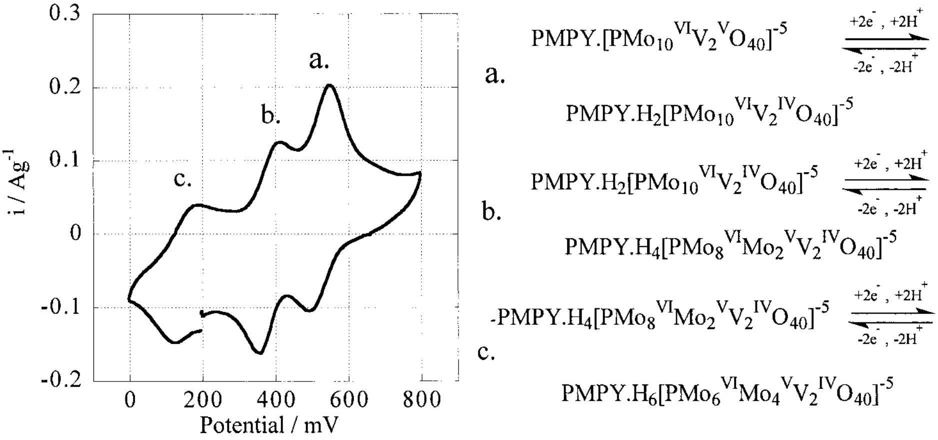

Figure 2. Carbon paper with a poly(*N*-methylpyrrole) coating doped with dodecamolybdo-divanadophosphoric acid (0.1 M H_2SO_4 against Ag / AgCl), with the accompanying mechanism for the electron transfer reactions.

Cyclic voltammetry of the electrodes revealed peaks associated with the three heteropolyacid electron transfers involving $2e^-$ exchanges which completely dominated the polypyrrole and poly(*N*-methylpyrrole) peaks (Figure 2). Lira-Cantú and co-workers have previously observed these peaks associated with encapsulated heteropolyacid.[8,9] The overall charge of the heteropolyacid is maintained as the polymer stabilises *via* proton transfer from the backbone.[10]

Lowering of the scan rate resulted in an increase of the reversibility of the system; for example, the polypyrrole electrode doped with the dodecamolybdophosphoric acid had peak separations, ΔEp, of ≈ 200 mV at a scan rate of 100 mV s^{-1} which reduced to ≈ 40 mV at 1 mV s^{-1}. Capacitances for the electrodes were calculated from the division of the mean of the anodic and cathodic current peaks (*I* in A) by the scan rate (*s*, in mV s^{-1}) (Equation 1).

$$C = \frac{i}{s} \qquad (1)$$

The highest capacitance obtained was given by the carbon paper coated with the 10-molybdo-2-vanadophosphoric acid-doped polypyrrole at 1 mV s^{-1}. The values were 776 F g^{-1} (per mass of active polymer) and 0.79 F cm^{-2} (of electrode area).

Fabrication and results from membrane electrode assemblies (MEA)

Disks were cut (1.3 cm in diameter) from the polymer-coated carbon papers and then pre-treated by boiling in deionised water for 30 minutes. Nafion® 115 was cut into squares (3 cm x 3 cm) boiled successively in hydrogen peroxide (30%), nitric acid (4 mol dm^{-3}) and then repeatedly refluxed in deionised water. The treated Nafion® was then placed between two electrode disks and pressed at 75 °C for 15 minutes under 5 tonnes using a KBr disk press and thermocouple-controlled drum heaters. The MEA was cut from excess Nafion® and then re-hydrated to a required water content using either 100% relative humidity (placed in a sealed container over a dish of water) or wet (re-hydrated in a dish of deionised water).

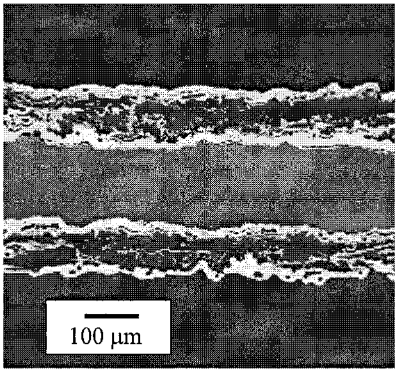

Figure 3. Scanning electron microscopy (secondary electron image) of the cross-section of a typical membrane electrode assembly. With carbon paper electrodes coated with polypyrrole doped with dodecamolybdophosphoric acid.

Cross-sectional analysis (Figure 3) revealed good contact between the electrodes and the Nafion® with an MEA thickness of 300 μm. The polymer coat (≈15 μm thick) did not appear to penetrate the internal surfaces of the carbon paper. The hot pressing technique reduced the thickness of the carbon weave by 30%, from ≈ 90 to 60 μm. Nafion was reduced to 115 μm, which is lower than the thickness obtained from uncompressed Nafion at 0% relative humidity.

MEAs were placed into an in-house built test cell, placed under a torque of 5 N m and tested using a.c. impedance analysis and charge / discharge cycling techniques. Charge / discharging cycling was observed over 200 cycles at ±1 mA. The a.c. impedance of the MEA was taken *in situ* at the beginning and end of the 200 galvanic cycles.

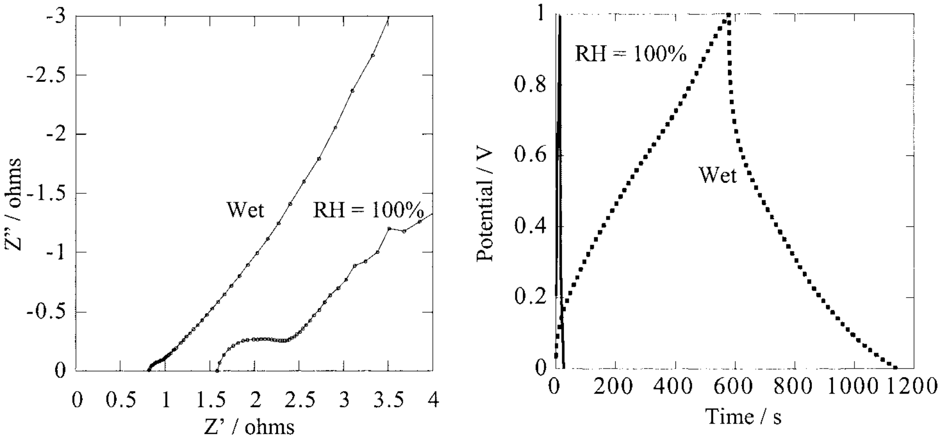

Figure 4. A.c. impedance plot and charge / discharge curves of MEA. Electrode coating: polypyrrole doped with dodecamolybdo-divanadophosphoric acid. Run under wet and RH = 100% conditions.

The resistance relating to the Nafion® electrolyte, the interfacial contact between the membrane and the electrode resistance all increased on decreasing relative humidity or after galvanic cycling (Figure 4). The MEAs which were run under wet conditions were found to give higher values for specific capacitance, specific power and specific energy when compared with the MEA run at RH = 100% (Figure 4). Improved discharge characteristics were observed from the MEA, which incorporated polypyrrole electrodes.

Conclusion

Electrodes were made which showed a suitable morphology for good contact with Nafion® electrolyte. Cyclic voltammetry showed the strong influence of the heteropolyacid encapsulated in the electrodes, responses which dominated the CVs. The heteropolyacid dodecamolybdo-divanadophosphoric acid combined with polypyrrole led to high values of capacitance per unit mass of active polymer. Charge / discharge and a.c. impedance tests on MEA devices showed that the most favoured systems were run under wet conditions and employed polypyrrole doped with heteropolyacids.

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