High performance conducting polymer supported oxygen reduction catalysts

Zhigang Qi and Peter G. Pickup*

Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7.
E-mail: ppickup@morgan.ucs.mun.ca

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Conducting poly(3,4-ethylenedioxythiophene)/poly(styrene-4-sulfonate) composites containing Pt catalyst nanoparticles produce currents as high as 0.4 A cm^{-2} at 0.5 V *vs.* NHE for oxygen reduction in gas diffusion electrodes.

Composites consisting of a conducting polymer and a polyanion could be the ideal catalyst supports for proton exchange membrane fuel cells (PEMFC) because they possess both high electronic and proton conductivities as well as being permeable to gases and water. We have reported the chemical deposition of Pt and platinum oxide nanoparticles on a polypyrrole/poly(styrene-4-sulfonate) (PSS) composite, and demonstrated oxygen reduction performances superior to those previously obtained with conducting polymer supported catalysts.[1,2] However, one of the biggest challenges we faced was that the electronic conductivity of the polypyrrole was seriously degraded by the deposition of the catalyst particles under both reducing (formaldehyde, hydrogen, or citrate) and oxidizing conditions (H_2O_2).[1] We found that polyaniline also suffered irreversible conductivity losses when catalysed under similar conditions, and so we turned our attention to poly(3,4-ethylenedioxythiophene) (PEDOT) which is reported to be more stable than polypyrrole under oxidizing conditions[3] and at elevated temperatures.[4] Preliminary results on the chemical synthesis of PEDOT/PSS particles and their use as a catalyst support are reported here. PSS was used as the counter anion during synthesis so that the resulting polymer composite would be a cation (proton) conductor.[5]

Since the EDOT monomer has a low solubility in water (2.1 g l^{-1} at 20 °C) and NaPSS is not soluble in suitable organic solvents, polymerization from solution can only be done under dilute conditions. This is known to lead to conducting polymers with inferior conductivities[6] and this was confirmed in our preliminary experiments. A better approach was to polymerize EDOT from a suspension in NaPSS(aq). In a typical procedure, 0.8 ml of EDOT (7.5 mmol; Bayer) was added to 15 ml of 0.1 M NaPSS (1.5 mmol; Aldrich), and the mixture was stirred vigorously for 30 min. EDOT dispersed much better in 0.1 M NaPSS than in pure water, and this is a key factor in the formation of highly conducting PEDOT/PSS. Upon addition of 15.3 g $Fe(NO_3)_3 \cdot 9H_2O$ (38 mmol) in 5 ml of water, EDOT polymerized immediately leading to a dark blue mixture. A deep blue powder was collected by filtration after 2 h and dried overnight at 50 °C under vaccum. The electronic conductivity of this composite measured with a four-point probe assembly described elsewhere[7] was 9.9 S cm^{-1}. For comparison, the conductivity of carbon black (Vulcan XC-72R) measured similarly was 3.0 S cm^{-1}. After 11 months storage in air, the conductivity of the PEDOT/PSS sample had dropped to 2.2 S cm^{-1}.

Pt deposition (20% by mass) on this PEDOT/PSS composite was then performed in the following way. 0.2010 g PEDOT/PSS and 0.1330 g $H_2PtCl_6 \cdot xH_2O$ were stirred in 50 ml of aqueous formaldehyde (18%) for 1 h at room temperature. The mixture was then heated to reflux for 1 h, followed by filtration and vacuum drying. A 95% yield of Pt/PEDOT/PSS was obtained. Transmission electron microscopy and X-ray diffraction revealed that this deposition method produces Pt particles on the polymer composite with an average diameter of *ca.* 4 nm.

The electronic conductivity of the catalyzed material was 4.0 S cm^{-1} (Vulcan XC-72R catalyzed with 20% Pt (Electrosynthesis) gave a conductivity of 3.3 S cm^{-1} under the same conditions). Thus PEDOT/PSS is relatively stable to the reducing conditions (formaldehyde) required for Pt decomposition. This is in dramatic contrast to other conducting polymers such as polypyrrole and polyaniline whose conductivities decreased by 3–4 orders of magnitude when refluxed in formaldehyde for 15 min.

After 11 months storage in air, the conductivity of the Pt catalysed PEDOT/PSS sample had dropped to 5 mS cm^{-1}. Other Pt/PEDOT/PSS samples were found to be stable over extended periods when stored in methanol, suggesting that the instability in air is due to overoxidation[8] by O_2 which is activated by the Pt particles. This instability must clearly be overcome before conducting polymer supported catalysts can be considered as viable materials for commercial applications.

Since it has been reported that PEDOT has good stability under oxidizing conditions, we attempted to deposit platinum oxide on PEDOT/PSS *via* the oxidation of $Na_6Pt(SO_3)_4$ by 0.35% H_2O_2.[9] However, we found that the polymer composite was destroyed by the H_2O_2, and only a *ca.* 3% yield of a poorly conducting material was obtained.

A number of Pt catalysed (formaldehyde reduction of H_2PtCl_6) polymer composites were tested for oxygen reduction in a cell[2,7] designed to approximate the conditions in an ambient temperature PEMFC. For comparison, a commercial catalyst (Electrosynthesis; 20% Pt on Vulcan XC-72R carbon black) was tested in the same way. Polarization curves for the catalysed polymers and Pt on XC-72R are shown in Fig. 1. The best Pt/PEDOT/PSS electrode achieved a current density of 0.47 Å cm^{-2} at 0.45 V (*vs.* NHE), which is much better than any previously reported conducting polymer supported system.[2] This electrode gave comparable performance to one with the commercial carbon supported catalyst although a higher Pt

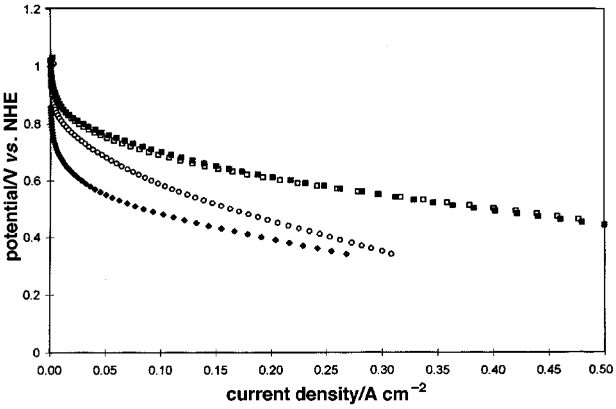

Fig. 1 Polarization curves for oxygen reduction in gas diffusion electrodes at ambient temperature (*ca.* 25 °C). The catalyst was mixed with a PTFE binder and sandwiched between carbon fibre paper exposed to O_2 (1 atm) and a Nafion membrane in contact with 1 M H_2SO_4(aq) containing a reference and counter electrode. (■) Commercial 20% Pt on carbon (0.31 mg Pt cm^{-2}), (□) 37% Pt on PEDOT/PSS prepared at high dilution (0.89 mg Pt cm^{-2}), (○) 19% Pt on PEDOT/PSS prepared at high dilution (0.29 mg Pt cm^{-2}), (◆) 20% Pt on emulsion polymerized PEDOT/PSS (0.40 mg Pt cm^{-2}). Data collected after 2 s at each potential.

loading was required (there was no significant dependence on Pt loading for the commercial catalyst for loadings from 0.2 to 1.0 mg cm^{-1}). Surprisingly, the catalysts prepared with PEDOT/PSS synthesized under dilute conditions performed significantly better than that prepared with the PEDOT/PSS synthesized from an EDOT suspension, despite their lower electronic conductivities (*ca.* 0.3 S cm^{-1}). The active Pt areas and proton conductivities of the two catalysts were similar, suggesting that the different performances are due to different oxygen permeabilities. The factors that determine the activities of Pt/PEDOT/PSS catalysts are under current investigation and will be discussed in detail elsewhere.

The results presented here show that high performance fuel cell catalysts can be prepared with conducting polymer supports. Further optimization can be expected to lead to catalysts that are competitive with the current state of the art in PEMFC catalysts. However, a significant problem that must be overcome is the long term stability of the conducting polymer support in the presence of oxygen and catalytic Pt particles.

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Notes and references

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