

Short communication

Pt/C/MnO₂ hybrid electrocatalysts for degradation mitigation in polymer electrolyte fuel cells

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Abstract

Pt/C/MnO₂ hybrid catalysts were prepared by a wet chemical method. Pt/C electrocatalysts were treated with manganese sulfate monohydrate (MnSO₄·H₂O) and sodium persulfate (Na₂S₂O₈) to produce MnO₂. The presence of MnO₂ was confirmed by FTIR spectroscopy. Rotating ring–disk electrode (RRDE) experiments were performed on electrodes prepared using the hybrid electrocatalysts to estimate the amount of hydrogen peroxide (H₂O₂) formed during the oxygen reduction reaction (ORR) as a function of MnO₂ content. Pt/C/MnO₂ (5% by weight of MnO₂) hybrid electrocatalysts produced 50% less hydrogen peroxide than the baseline Pt/C electrocatalyst. The hybrid electrocatalysts were used to prepare membrane electrode assemblies that were tested at 90 °C and 50% RH at open circuit with pure hydrogen as fuel and air as the oxidant. The fluoride ion concentration was measured using an ion selective electrode. The concentration of F⁻ in the anode condensate over 24 h was found to be reduced by a factor of 3–4 when Pt/C/MnO₂ replaced Pt/C as the catalyst. Through cyclic voltammetry and RRDE kinetic studies, the lower ORR activity of the acid treated hybrid electrocatalysts was attributed to catalyst treatment with acid during MnO₂ introduction. The activity of the hybrid catalyst was improved by switching to a water-based synthesis.

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1. Introduction

Several reports on polymer electrolyte fuel cells (PEFCs) have shown that components of membrane electrode assemblies (MEAs) deteriorate during long-term operation [1–8]. One of the most serious issues is the deterioration of perfluorinated ionomer membrane used as the solid electrolyte [5–8]. Hydrogen peroxide can be formed in three ways within an operating fuel cell: (1) electrochemical two electron reduction of oxygen at the cathode; (2) chemical combination of crossover oxygen and hydrogen at the anode; (3) chemical combination of crossover hydrogen and oxygen at the cathode. It has been shown that HO• and HO₂• radicals produced by reaction of hydrogen peroxide with trace metal ions at the electrode and electrolyte of the fuel cell are responsible for membrane degradation [9–11]. Further evidence for this mechanism is the formation of hydrogen per-

oxide (H₂O₂) as detected in product water [12]. Degradation of the electrolyte membrane causes membrane thinning or pin-hole formation that can result in a significant loss in the performance.

The electrolyte membrane deterioration during operation of the cell is more pronounced under low humidification conditions. It has also been reported that the degradation is more significant under open-circuit conditions without net current [13]. PEFCs usually employ very thin electrolyte membranes (25–50 μm) to reduce the ionic resistance. Hence, despite the relative impermeability of the electrolyte membrane, reactant gas crossover is inevitable in PEFCs. But with increasing gas crossover, the rate of degradation is reported to increase [14]. This is because larger crossover leads to more hydrogen peroxide formation by chemical combination. It is therefore evident that the issue of hydrogen peroxide formation in the fuel cell electrodes needs to be addressed. Specifically, it is desirable to minimize the concentration of hydrogen peroxide in the fuel cell electrodes.

Three approaches can be used to minimize the effect of reactive oxygen species in a fuel cell: (i) the use of free radical

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scavengers; (ii) the use of dispersed peroxide decomposition catalysts within the electrolyte; (iii) the use of dispersed peroxide decomposition catalysts in the electrodes. The first approach can only delay the onset of degradation for a definite period due to steady consumption of the scavenger molecules, while the second approach does not eliminate reactive oxygen species before they enter the membrane. The third approach, hitherto unreported, is examined in this study. A peroxide decomposition catalyst (MnO_2) is incorporated within the anode and cathode electrocatalysts to yield hybrid electrodes. These electrodes should facilitate both electrochemical oxygen reduction and hydrogen peroxide decomposition to water and oxygen. By lowering hydrogen peroxide concentration within the electrode, the rate of generation of reactive oxygen species can also be minimized. The present study is aimed at validating this approach by synthesizing hybrid electrocatalysts (Pt/C-MnO_2 composites) and evaluating their efficacy in: (1) mitigating the generation of hydrogen peroxide and (2) lowering the rate of membrane degradation. The former is estimated through RRDE experiments by estimating the percentage of hydrogen peroxide detected at the ring during oxygen reduction. The latter is estimated through MEA studies; wherein the amount of fluoride ions released by the membrane is estimated after a specific operating period.

2. Experimental

A method similar to that one described in Zhang et al. [15] was used for the preparation of Pt/C/MnO_2 composite materials. Pt/C (40% by weight Pt loading; Alfa Aesar) powder was first treated in a mixture of concentrated H_2SO_4 (95–98%; Sigma–Aldrich) and HNO_3 (redistilled 99.9%; Sigma–Aldrich) with the volume ratio 3:1 to obtain better dispersion. This is a harsh step (in terms of potential detrimental effect on catalytic activity), but was used to ensure that the catalyst powder was made hydrophilic and that MnO_2 was well dispersed. Manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 99%; Sigma–Aldrich) powder was added to the catalyst dispersion followed by stirring for 5 h. Finally, sodium persulfate powder ($\text{Na}_2\text{S}_2\text{O}_8$ 98%; Sigma–Aldrich) was added to the beaker and the contents stirred overnight. The modified Pt/C was recovered using a centrifuge, rinsed with deionized water until the wash water pH was between 5 and 6 and dried under vacuum. The MnO_2 loading was controlled by adding appropriate amounts of manganese sulfate. Samples with 1%, 5%, 10% and 15% by weight of MnO_2 were prepared. Hybrid catalyst samples were also prepared without exposing the Pt/C catalyst to the acid by eliminating the acid treatment step and carrying out the synthesis in an aqueous environment.

Infrared transmission spectra were determined for each catalyst using a Thermoelectron Nicolet Spectrometer IR100. The total number of scans was 64 and the IR spectrum was obtained from 4000 to 400 cm^{-1} .

The oxygen reduction reaction on these catalysts was analyzed using the rotating ring–disk electrode (RRDE) technique [16]. The RRDE consisted of a glassy carbon disk and a platinum ring. Thin layers of the material to be tested were applied to the glassy carbon disk. The preparation of the electrode layer was as follows: 0.1 g of the sample was added to 10 cm^3 of

water and 0.86 g of 5% Nafion® dispersion (Solution technologies, Mendenhall, PA). The mixture was stirred for 24 h. Twenty microlitre of the dispersion was transferred to the disk electrode using a micropipette (Edvotek 10–100 μl , Fisher Scientific). The dispersion spread across the surface of the disk and the surface was allowed to dry prior to use.

The RRDE studies were conducted using a Pine analytical rotator (Model AFMSRX) and a three-electrode electrochemical cell that had a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the counter-electrode. The electrolyte used was 0.5 M sulfuric acid. A multi-channel potentiostat (Solartron Analytical; model 1480 multistat) was used to independently control/measure ring and disk current and potential.

The following procedure was used during the oxygen reduction experiments: First, the sulfuric acid solution was purged with nitrogen for 30–40 min and the ring and disk potentials was cycled between -0.23 and 1 V versus SCE. The solution was then purged with oxygen. The ring potential was held constant at 1 V versus SCE, while the disk potential was varied from 1 V versus SCE to 0 V versus SCE at a sweep rate of 10 mV s^{-1} . The ring and disk currents were recorded. The experiments were performed at 0, 250, 500, 750 and 1000 rpm for each sample. The procedure was then repeated for the other samples. The experiments were repeated at least three times for each catalyst sample to ascertain the precision of the measurement. The data is reported as the average value along with the standard error.

To test the efficacy of the hybrid catalysts, membrane electrode assemblies were prepared with Pt/C and $\text{Pt/MnO}_2/\text{C}$ (1% by weight of MnO_2) catalysts at the anode and cathode. Catalyst ink was prepared by mixing 0.36 g of catalyst, 3.1 g of 5% Nafion® dispersion and 6 cm^3 of methanol. The catalyst was wetted by adding a few drops of water before Nafion® or methanol were added to minimize the chance of fire. The ink was stirred for 24 h before use. MEAs were prepared by spraying successive layers of catalyst ink directly onto either side of the membrane. An IR-lamp was used to dry the MEA prior to the application of each layer. A PTFE mask was employed to maintain the active area of the MEA at 5 cm^2 . After both the anode and cathode catalyst layers were applied, the MEA was hot-pressed at 120°C and 10 atm. The overall loading of each electrode was estimated gravimetrically and was maintained at $7 \pm 1\text{ mg cm}^{-2}$. The platinum content in the Pt/C catalyst is 40% by weight and the Nafion® loading was maintained at 30% by weight. Thus, the platinum loading on each electrode in the MEA was $0.4 \pm 0.05\text{ mg cm}^{-2}$.

The MEAs were assembled in a 5 cm^2 fuel cell hardware containing serpentine flow fields. Two $375\text{ }\mu\text{m}$ thick gas diffusion layers (Sigracet 10BB) were used during assembly. The assembly was sealed using two $250\text{ }\mu\text{m}$ thick PTFE gaskets. The fuel cell was tested at open circuit at 90°C and 50% RH. Air was used as the oxidant at the cathode (flow rate = 0.2 slpm) and hydrogen was used as the fuel at the anode (flow rate = 0.2 slpm). The inlet gases were humidified by controlling the anode and cathode saturator dew points at 60°C . The test was run for 24 h for each MEA and the anode and cathode condensates were independently collected in cold-traps. The fluoride ion concentrations in

the condensate water were measured using a fluoride ion selective electrode (Denver Instruments) that was freshly calibrated before each measurement.

3. Results and discussion

3.1. FTIR

FTIR spectroscopy (Fig. 1) was used to qualitatively confirm the presence of MnO₂ in the modified samples. For Pt/C/MnO₂, the FTIR spectrum shows features at 457 and 576 cm⁻¹ that are very close to those reported previously for Mn–O bond vibrations in manganese oxide [17–20]. The spectra are representative of all samples prepared with MnO₂. These features are absent in the control Pt/C sample.

3.2. RRDE results: hydrogen peroxide formation on Pt/C and Pt/C–MnO₂ catalysts

The percentage of H₂O₂ detected at the ring during the reduction of oxygen ($X_{\text{H}_2\text{O}_2}$) at the disk can be calculated using the following equation [16]:

$$X_{\text{H}_2\text{O}_2} = \frac{2I_{\text{R}}/N}{I_{\text{D}} + (I_{\text{R}}/N)} \times 100$$

where I_{R} = ring current (a measure of hydrogen peroxide formation); I_{D} = disk current (measure of oxygen consumption by reduction); N = collection efficiency (function of geometric properties of the electrode).

For the electrode used in this study, the value of N was calculated to be 0.23. Prior studies have confirmed that the theoretically calculated value is very close to the value obtained experimentally by studying a standard redox couple (ferrocyanide–ferricyanide) for the RRDE geometry used in this study [21].

The amount of hydrogen peroxide detected at the ring for the baseline Pt/C catalyst was between 1.5% and 2% in the potential range 0.55–0.25 V versus SHE. This is consistent with values previously reported [21]. However, even these low percentages can be detrimental from the viewpoint of membrane degradation as a small number of free radicals generated from the peroxide produced are sufficient to initiate and sustain membrane

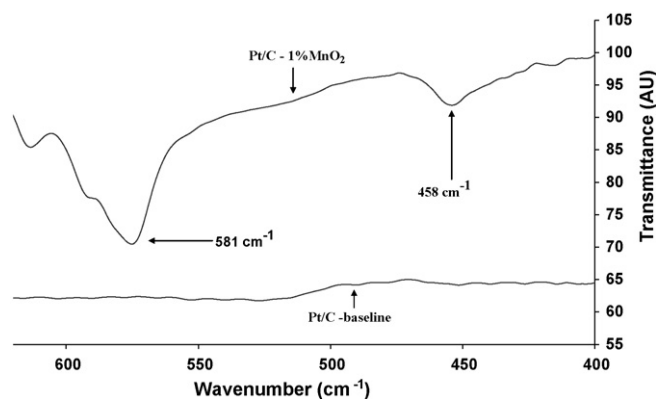


Fig. 1. IR spectra of baseline Pt/C and Pt/C–1% MnO₂ hybrid electrocatalysts.

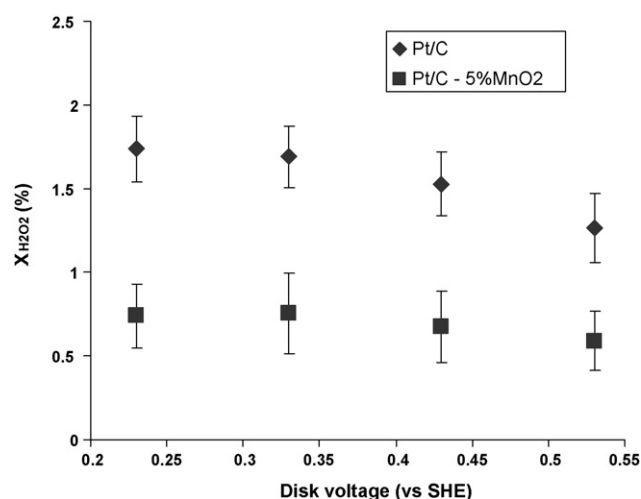


Fig. 2. RRDE results: percentage of H₂O₂ produced during oxygen reduction using Pt/C (baseline) and Pt/C–5% MnO₂ hybrid electrocatalysts (temperature: room temperature, rotation rate: 500 rpm, electrolyte used: 0.5 M sulfuric acid, ring potential was held constant at 1 V vs. SCE, while disk potential was varied from 1 V vs. SCE to 0 V vs. SCE at a sweep rate of 10 mV s⁻¹).

degradation. The potential dependence in $X_{\text{H}_2\text{O}_2}$ observed is consistent with the fact that the amount of H₂O₂ formed electrochemically increases as the electrode potential is lowered further from the equilibrium potential for the two electron reduction of oxygen (0.695 V versus SHE). The Pt/C–1 wt% MnO₂ catalyst showed a 20–25% reduction in the amount of peroxide detected at the ring when compared to baseline Pt/C. Increasing MnO₂ loading in the hybrid electrocatalyst to 5 wt% resulted in a lowering of 50–60% in the amount of peroxide detected at the ring (Fig. 2). MnO₂ is known to be a good hydrogen peroxide decomposition agent [22,23] and hence it is believed that the MnO₂ in the hybrid catalyst decomposes the peroxide that is generated electrochemically before it reaches the ring. Increasing the MnO₂ loading further to 10% and 15% by weight resulted in peroxide detection at the ring that was comparable to the pure Pt/C electrocatalyst. No mitigation was seen for these compositions. These results suggest that introducing an optimal amount of a peroxide decomposition catalyst into Pt/C electrocatalysts will reduce the amount of hydrogen peroxide present in the electrode. The optimum formulation in this study is Pt/C–5 wt% MnO₂.

3.3. MEA results

The fluoride emission rates for Pt/C and Pt/C/MnO₂ electrocatalysts were obtained by testing four MEAs of each type (Fig. 3). The average fluoride emission in the anode condensate was significantly reduced (by a factor of 3–4) from 1.1 to 0.22 ppm. At the cathode, the reduction was more modest and a 30% drop in the average fluoride emission was observed. This result indicates that in addition to reducing the amount of hydrogen peroxide produced, the hybrid electrocatalyst lowers the rate of membrane degradation. The cathode potential was 200 mV lower for MEAs using the hybrid electrocatalysts and decreased during the test, despite similar hydrogen crossover currents being observed for MEAs prepared with base-

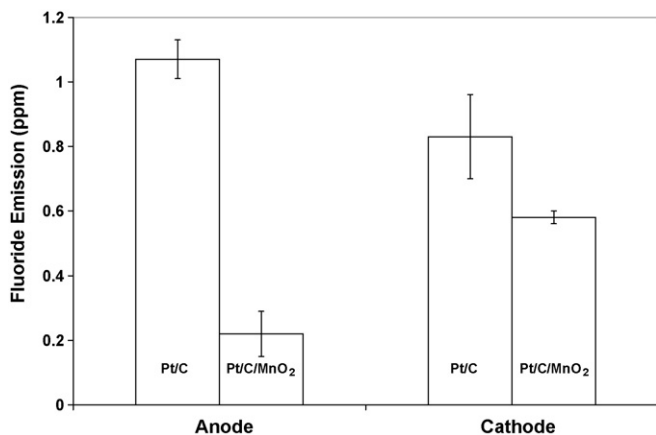


Fig. 3. Fluoride ion concentration rates measured at the anode and cathode condensates for Pt/C and Pt/C–1%MnO₂ catalysts during MEA testing (cell temperature: 90 °C, saturator temperature: 60 °C, corresponding to 30% inlet RH at both anode and cathode, anode gas: pure hydrogen; cathode gas: oxygen, gas flow rate: 0.2 slpm, experimental duration: 24 h).

line Pt/C and hybrid electrocatalysts. The low cathode potential was attributed to the loss of catalytic activity due to the MnO₂ preparation process, which involved suspension of the catalyst in acid during preparation. A further discussion of catalyst activity is presented in the following section.

3.4. Catalytic activity

The lower activity of the hybrid catalysts was confirmed by cyclic voltammetry measurements and kinetic measurements during the RRDE studies. To confirm that the lowering in activity was due to the treatment with acid and not due to MnO₂ addition, a Pt/C catalyst sample was exposed to the same acid treatment without addition of manganese precursors. The cyclic voltammograms for Pt/C (baseline), Pt/C exposed to acid, and Pt/C/MnO₂ hybrid electrocatalysts are shown in Fig. 4. The loadings of the samples were similar to one another and it is clearly seen that the electrochemically active surface area (ECA) is much smaller for the catalysts exposed to acid. To confirm that the loss of activity was indeed due to acid treatment, the mass

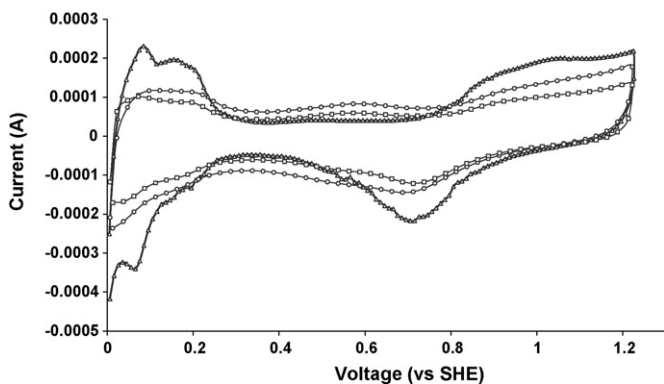


Fig. 4. Cyclic voltammograms for baseline Pt/C (Δ); acid treated Pt/C (\circ); acid treated Pt/C–5% MnO₂ hybrid electrocatalyst (\diamond) (temperature: room temperature, electrolyte used: 0.5 M sulfuric acid, disk potential cycled between –0.23 and 1 V vs. SCE, scan rate: 50 mV s^{–1}).

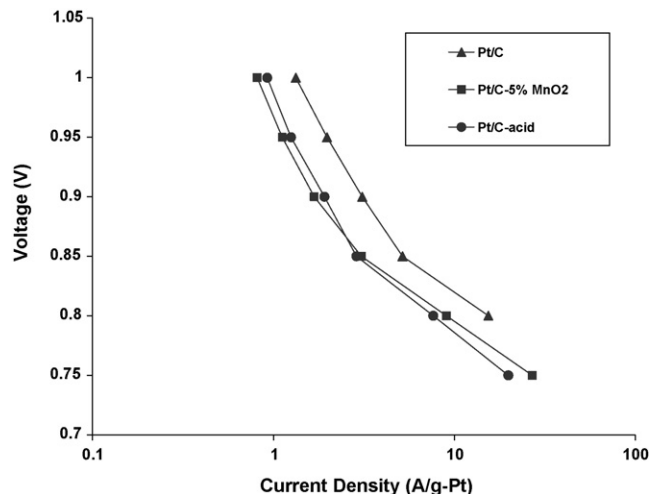


Fig. 5. Mass specific current densities obtained using Pt/C, acid treated Pt/C and Pt/C–5%MnO₂ hybrid electrocatalysts (temperature: room temperature, rotation rate: 500 rpm, electrolyte used: 0.5 M sulfuric acid, disk potential was varied from 1 V vs. SCE to 0 V vs. SCE at a sweep rate of 10 mV s^{–1}).

specific current densities for the three samples were examined (Fig. 5). It is seen that the samples treated with acid are less active than the pristine Pt/C sample, and that the mass specific current densities of the Pt/MnO₂/C hybrid catalysts lie right on top of the acid treated platinum catalyst. Tests performed on water-based hybrid catalysts show that eliminating the harsh acid treatment yielded hybrid electrocatalysts with ECA very similar to that of pristine Pt/C (Fig. 6). The mass specific current density of this catalyst at 0.95 V is only 10% less than that of pristine Pt/C. There remains scope for improvement in hybrid electrocatalyst activity.

Since MEA and RRDE studies were carried out in parallel, the electrocatalysts used for MEA studies had 1 wt% of MnO₂ as opposed to the RRDE studies derived optimum of 5 wt% of MnO₂. The low cathode activity of the MEAs with the hybrid electrocatalysts prompted us to stop MEA testing until an alternate route to synthesize the hybrid electrocatalyst could be

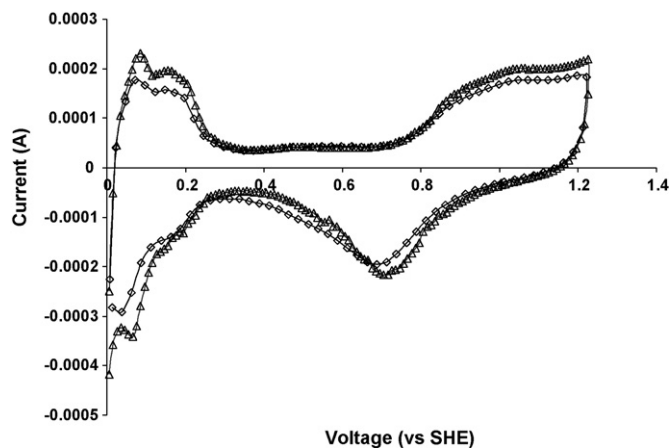


Fig. 6. Cyclic voltammograms for baseline Pt/C (Δ) and Pt/C–5% MnO₂ hybrid electrocatalyst (\diamond) prepared using a water-based method (temperature: room temperature, electrolyte used: 0.5 M sulfuric acid, disk potential cycled between –0.23 and 1 V vs. SCE, scan rate: 50 mV s^{–1}).

developed. Hence, MEAs with other MnO₂ compositions were not prepared or tested in this study. It is however, promising to note that significant degradation mitigation is observed even with the non-optimal MnO₂ loading. It should be stressed that the RRDE environment and fuel cell environment are markedly different and that the optimal decomposition catalyst loading for the two may well differ. The purpose of conducting tests in these different environments was not to obtain concordance, but rather to obtain two different measures: (1) amount of peroxide detected at the ring during electrochemical oxygen reduction and (2) amount of fluoride ions released during fuel cell operation.

4. Conclusions and future directions

A wet chemical method was used to prepare Pt/C/MnO₂ hybrid electrocatalysts. The presence of MnO₂ in these catalysts was confirmed by FTIR spectroscopy. The percentage of H₂O₂ produced during the oxygen reduction reaction on these catalysts was examined through RRDE measurements. It was shown that the addition of 5 wt% of manganese dioxide to Pt/C electrocatalyst resulted in a 50–60% reduction (over baseline Pt/C) in percentage of H₂O₂ detected at the ring. Hybrid electrocatalysts with 1% of MnO₂ also exhibited a 20–25% lowering in percentage of H₂O₂ detected at the ring. Catalysts with 10% and 15% by weight of MnO₂ showed no improvement over baseline Pt/C. These results suggest that the addition of an optimal amount of peroxide decomposition catalyst will decompose hydrogen peroxide and can help mitigate membrane degradation. To confirm that the hybrid electrocatalysts do lower the rate of membrane degradation, MEAs were prepared using baseline Pt/C and Pt/C–1 wt% MnO₂ hybrid electrocatalysts in the electrodes. The condensate water at the anode and cathode were analyzed for F[−] ion concentration for each type of MEA. The hybrid electrocatalyst demonstrated a three to fourfold lowering in the average F[−] ion concentration in the anode condensate. A 30% reduction was also observed in the average F[−] ion concentration at the cathode condensate. The incorporation of MnO₂ required treating the Pt/C electrocatalyst with acid to improve dispersion and ensure uniform distribution of MnO₂. However, this had a detrimental effect on catalytic activity. The addition of MnO₂ was discounted as the source of loss of catalytic activity by testing a sample of Pt/C that was subjected to the same acid treatment. Cyclic voltammetry and RRDE kinetic studies showed that the acid treatment was the primary factor responsible for activity loss. Tests with hybrid catalysts prepared using a water-based route showed that these catalysts had higher ECA – similar to that of pristine Pt/C – and higher mass specific current densities than their acid treated counterparts.

Our research is now focused on: (1) studying the extended stability of the hybrid electrocatalysts; (2) studies with oxides other than MnO₂; (3) obtaining a better understanding of the mechanism of operation of the hybrid electrocatalysts. Results from these studies will be reported in the future.

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References

- [1] M.S. Wilson, F.H. Garzon, K.E. Sickafus, S. Gottesfeld, *J. Electrochem. Soc.* 140 (1993) 2872.
- [2] M. Schulze, A. Schneider, E. Gülzow, *J. Power Sources* 127 (2004) 213.
- [3] S.D. Knights, K.M. Colbow, J. St-Pierre, D.P. Wilkinson, *J. Power Sources* 127 (2004) 127.
- [4] J. Xie, D.L. Wood, K.L. More, P. Atanassov, R.L. Borup, *J. Electrochem. Soc.* 152 (2005) A1011.
- [5] A. Pozio, R.F. Silva, M.D. Francesco, L. Giorgi, *Electrochim. Acta* 48 (2003) 1543.
- [6] T.A. Zawodinski, J. Xie, D.L. Wood, D.M. Wayne, P. Atanassov, R.L. Borup, *J. Electrochem. Soc.* 152 (2005) A104.
- [7] D.E. Curtin, R.D. Lousenberg, T.J. Henry, P.C. Tangeman, M.E. Tisack, *J. Power Sources* 131 (2004) 41.
- [8] J. Yu, T. Matsuura, Y. Yoshikawa, M.N. Islam, M. Hori, *Electrochem. Solid State Lett.* 8 (2005) A156.
- [9] H. Wang, G.A. Capuano, *J. Electrochem. Soc.* 145 (1998) 780.
- [10] T.J. Schmidt, U.A. Paulus, H.A. Gasteiger, R.J. Behm, *J. Electroanal. Chem.* 508 (2001) 41.
- [11] C. Lu, C. Rice, R.I. Masel, P.K. Babu, P. Waszczuk, H.S. Kim, E. Oldfield, A. Wieckowski, *J. Phys. Chem. B* 106 (2002) 9581.
- [12] N.A. Aweir, *Eur. Polym. J.* 14 (1978) 9.
- [13] E. Roduner, A. Panchenko, H. Dilger, E. Möller, T. Sixt, *J. Power Sources* 127 (2004) 325.
- [14] F.N. Büchi, B. Gupta, O. Haas, G.G. Scherer, *J. Electrochim. Acta* 40 (1995) 345–353.
- [15] X.G. Zhang, C.M. Shen, H.L. Li, *Mater. Res. Bull.* 36 (2001) 541.
- [16] M. Inaba, *Proceedings of the 14th International Conference on the Properties of Water and Steam in Kyoto*, 2001.
- [17] L. Zhang, Z.-H. Liu, X. Tang, J. Wang, K. Ooi, *Mater. Res. Bull.* (January 2007), corrected proof.
- [18] L. Li, Y. Chu, Y. Liu, L. Dong, *Mater. Lett.* 61 (2007) 1609–1613.
- [19] R. Yang, Z. Wang, L. Dai, L. Chen, *Mater. Chem. Phys.* 93 (2005) 149–153.
- [20] H.-E. Wang, D. Qian, Z. Lu, Y. Li, R. Cheng, W. Zhang, *Cryst. Growth*, (January 2007), corrected proof.
- [21] T. Skiba, Master's Thesis, University of Connecticut, December 2004.
- [22] M.W. Rophael, N.S. Petro, L.B. Khalil, *J. Power Sources* 22 (1988) 149–161.
- [23] J. Petlicki, D. Palusova, T.G.M. Van de Ven, *Ind. Eng. Chem. Res.* 44 (2005) 2002–2010.