Influence of Ammonium on Platinum Surfaces in Acidic Solutions

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PEM fuel cell performance is affected by traces of ammonia (≈10 ppm) in the fuel gas as shown by Uribe *et al.* [1]. Uribe *et al.* [1] concluded that the performance decay was due to absorption of ammonia by the ionomer in the anode electrode layer, which lowered the ionic conductivity of the ionomer. Effects of ammonium on bulk membrane properties of Nafion® 117 (water content, swelling properties and conductivity) have been reported previously [2].

Ammonia (or ammonium) may also have other effects on the PEM fuel cell than decreased ionic conductivity. In this paper we study the influence of ammonium on a polycrystalline platinum surface in acidic electrolytes. Previous relevant studies have focused on oxidation of ammonia in alkaline electrolytes [3-5] and reduction of nitric oxides in acidic electrolytes [6], and it has been found, using different methods like FTIR [6] and DEMS [4,5], that ammonia is oxidized to nitrogen at lower potentials than about 0.8 V_{RHE} and to nitrogen oxides at higher potentials. Nitrogen oxides have been found to be reduced to ammonia at low potentials [4]. There are reports that ammonium is electrochemically inactive [3], but no details have been reported. The behavior of ammonium on either fuel cell electrode is of interest both because it may poison the Pt surfaces, but also since oxidation of ammonium may be an important factor for how quickly a fuel cell can recover it's original performance after exposure to ammonia.

Experimental procedure. Solutions were prepared using sulfuric acid (Fisher, ACS Plus grade) and as received Ammonium Sulfate (Fisher ACS grade) using purified water from a MilliQ UV-PLUS system. Cyclic voltammograms were recorded using a PAR 273 potentiostat. The reference electrode used was a Reversible Hydrogen Electrode (RHE) in the same solution. The working electrode was a Pt-wire (99.95 % Pt, Alfa Æsar) with an estimated roughness factor of 1.3 based on hydrogen adsorption area in pure sulfuric acid (210 $\mu C/cm^2$). The solutions were de-aerated by Ar prior to measurements and kept under Ar atmosphere.

Results. As shown in Figure 1 we see that several features of the CV obtained in pure sulfuric acid is altered by addition of ammonium sulfate (refer to Figure 1 for numbering of features in the CV). The decrease in the hydrogen adsorption peak 1 is compensated by an increased reduction current under peak 2. Shingaya *et al.* [7] attributed a similar effect observed on Pt(111) in 0.1 M H_2SO_4 + 0.1 M NH_3 to coadsorption of ammonium and HSO_4^-. There is also a slight change in region 3, but this is also seen when adding sodium sulfate, consistent with findings of Huang *et al.* [8]. The formation of an oxide layer on Pt is also affected (less steep shoulder and also loss of the two broad peaks observed in pure acid (region 4)). The platinum oxide reduction peak is also broadened and shifted to slightly lower potentials (region 5). These effects will be further investigated and the results presented.

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[1] F.A. Uribe, S. Gottesfeld, and T.A. Zawodzinski, Jr., *J. Electrochem. Soc.*, **149**, A293 (2002).
[2] R. Halseid, P. J. S. Vie, and R. Tunold, Abstract 829 presented on at the 202nd meeting of ECS, 2002.
[3] H. Gerischer and A. Mauerer, *J. Electroanal. Chem.* **25**, 421 (1970).
[4] S. Wasmus, E.J. Vasini, M. Krause, H.T. Mishima, and W. Vielstich, *Electrochim. Acta*, **39**(1), 23 (1994).
[5] A.C.A. de Vooys, M.T.M Koper, R.A. van Santen, and J.A.R. van Veen, *J. Electroanal. Chem.* **506**, 127 (2001).
[6] A. Rodes, R. Gómez, J.M. Orts, J.M. Feliu, J.M. Pérez, and A. Aldaz, *Langmuir*, **11**, 3549 (1995).
[7] Y. Shingaya, H. Kubo, and M. Ito, *Surf. Sci.*, **427-428**, 173 (1999).
[8] J.C. Huang, W.E. O'Grady, and E. Yeager, *J. Electrochem. Soc.*, **124**(11), 1732 (1977).

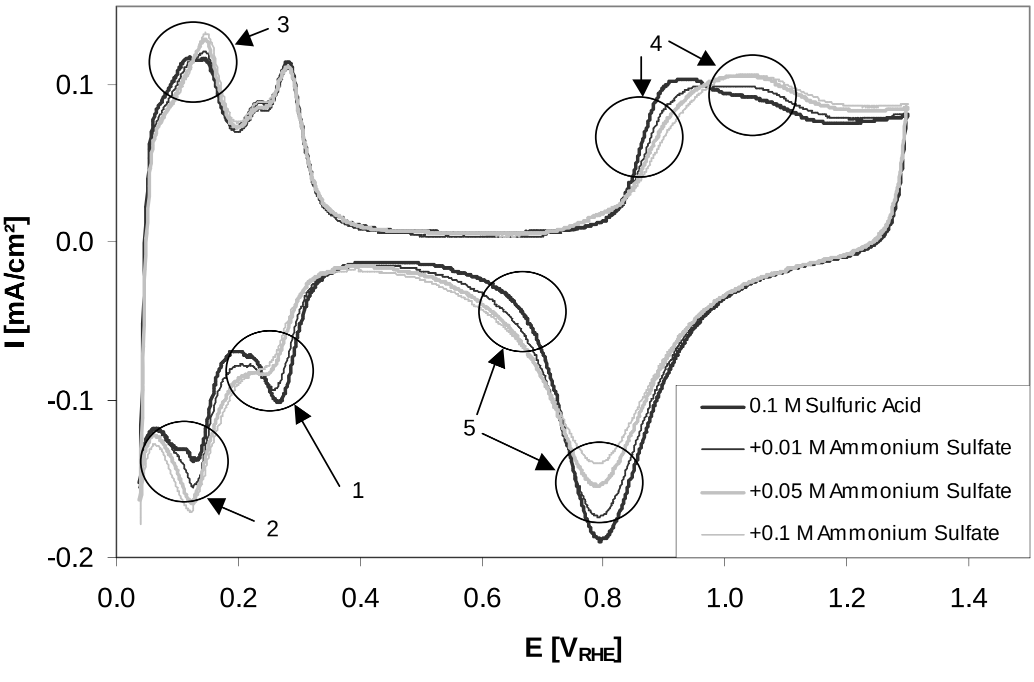

Figure 1. Cyclic voltammogram of Pt in 0.1 M sulfuric acid with different additions of ammonium sulfate. Room temperature, scan rate 100 mV/s.