

## A Fluorinated Ionic Liquid as a High-Performance Fuel Cell Electrolyte

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### Abstract

This is the first report of a fuel cell with a proton-conducting ionic liquid (pIL) electrolyte that outperforms one with aqueous concentrated (85%) phosphoric acid over all current densities. The new pIL, 2-fluoropyridinium triflate (2-FPTf), is a fluorinated pIL that was made by mixing equimolar amounts of 2-fluoropyridine and triflic acid. A Pt-catalyzed fuel cell fed dry hydrogen and oxygen gases was stable at 80°C with neat 2-FPTf as the electrolyte. The polarization curve showed more than 15% improvement in performance ( $> 0.1$  V cell voltage gain) compared to an identical fuel cell except with aqueous 85% phosphoric acid as the electrolyte. The stability of the fuel cell with 2-FPTf is attributed to it being a fluorinated electrolyte that does not wet Teflon. The improved fuel cell performance is attributed to low water-activity of the electrolyte leading to suppression of oxide formation on Pt and improved cathode performance. This was supported by the voltammetry of Pt in 2-FPTf electrolyte equilibrated with oxygen, which showed oxygen reduction begins near the thermodynamic limit of 1.2 V versus RHE at 80°C.

### Introduction

To achieve highly efficient performance, an acid fuel cell electrolyte needs to: have high proton conductivity, be stable under fuel cell operating conditions and allow hydrogen and oxygen to adsorb on electrocatalysts [1]. Recently, protic ionic liquids (pIL) have been suggested as a new class of electrolyte, that can be operated at higher temperatures (up to 120°C), because pILs do not need water to conduct proton. A pIL is a neat salt electrolyte that forms by proton transfer from a Bronsted acid to a Bronsted base and that is liquid at temperatures below 100°C. Fuel cells were reported to give higher efficiency operation when pILs were substituted for concentrated phosphoric acid [2], and the best performance was with pIL electrolytes that contained aliphatic amines and nitrates [2]. However fuel cells with these pILs demonstrated two undesirable behaviors: 1) the high performance was limited to lower current densities ( $< 10$  mA/cm<sup>2</sup>) due to mass

transport limitations, because these pIL electrolytes wet and flood Teflon-bound gas-fed electrodes, and 2) the high performance was short lived (on the order of hours) because these pILs were found to be unstable on Pt in the presence of oxygen and highly positive electrode potentials. Fluorinated hydrocarbons are well known for their oxidative stability. In an attempt to make stable pIL electrolytes, they are being prepared from fluorinated acid and base moieties, such as, the new pIL, 2-fluoropyridium triflate (2-FPTf) that is reported here.

Because protic salt electrolytes are non-aqueous electrolytes, they allow the possibility for highly efficient oxygen electroreduction and fuel cell performance, because oxygen adsorption and reduction on Pt can occur at potentials as high as 1.2V versus RHE. In an aqueous acid electrolyte, a platinum electrode will adsorb water and form Pt-hydroxide at around 0.8 V versus RHE and a compact Pt-oxide monolayer as the electrode is brought to higher oxidizing potentials. These hydroxide and oxide layers on Pt interfere with the adsorption of molecular oxygen. Oxygen reduction on platinum in an aqueous electrolyte can not occur until the surface platinum oxide species are reduced to expose metallic platinum [1,3] which occurs at high overpotentials for oxygen reduction ( $\leq 0.85$  V vs. RHE), which results in inefficient cathode and fuel cell performance. On the other hand, since a pIL electrolyte is free of reactive bulk water; the reaction between Pt and water is inhibited and the Pt stays oxide free. Accordingly, oxygen can be adsorbed and reduced on an oxide-free Pt surface in a pIL at potentials near the thermodynamic limit of 1.2V. Another intriguing possibility, when using a pIL electrolyte, is that non-Pt metal catalyst could be used in a fuel cell. Most metal corrosion is driven by a local cell process in which metal oxidation to metal-oxide occurs on one part of the metal surface and reduction of oxygen or proton on another part. This is usually driven by the highly negative free energy of metal-oxide formation as a metal reacts with water. Just as oxides do not form on Pt in protic salt electrolytes, because the activity of water is so low, then - for the same reason - practically no corrosion of any metal catalyst, including a non-noble metal whose oxidation potential is higher than the oxygen reduction potential (1.2 V vs. RHE), would be expected in a protic salt electrolyte.

Most interest is in developing fuel cells using a solid polymer electrolyte membrane (PEM); because liquid electrolytes can soften and weaken fuel cell structures and can also escape from a cell in a stack and form power-robbing short circuits. To make a protic salt membrane, a polymer with a covalently attached base (or acid) is reacted with an equivalent of acid (or base). However, due to complex current distribution in a solid ion conductor, it is difficult to use a reference electrode to study individual electrode potentials in a membrane fuel cell. On the other hand, the potential at the catalyst/electrolyte interface is readily interrogated with an electrode in a liquid salt electrolyte, and much can be learned about the fundamental properties of the catalyst/salt electrolyte interface with a pIL electrolyte. So although the pIL electrolytes are of interest in their own right, one motivation for studying the new pIL electrolytes is that they serve as convenient models for designing new protic salt membranes. The overall goal for developing a protic salt membrane is to obtain the structural stability of a PEM and the high performance of a pIL.

## Experimental

The 2-FPTf was synthesized as reported previously [4] by combining 1 mole of trifluoromethane sulfonic acid (TFMSA, also called triflic acid, Aldrich) with 1 mole of 2-fluoropyridine (Alfa Aesar) with the 2-fluoropyridine in a very slight (<1%) excess. Prior to the reaction, both reactants were purified by repeated distillation until they were clear and colorless. The 2-fluoropyridine was added drop wise to neat triflic acid in a glass vessel in a dry ice/acetone bath at  $-78^{\circ}\text{C}$ . The sample was dried at  $\sim 10$  Torr in a vacuum oven at  $90^{\circ}\text{C}$  for a period of 24 hours prior to using it in electrochemical experiments.

Cyclic voltammetry was conducted using a standard three electrode configuration and a Princeton Applied Research VMP2/Z potentiostat. The working and counter electrodes were 0.3mm diameter platinum wire. The volume of the electrolyte was 2.0 mL which was equilibrated with a dry research grade Argon or oxygen atmosphere over the electrolyte. To avoid junction potentials, the reference electrode was a reversible hydrogen electrode (RHE). The RHE was made by placing electrolyte into a glass tube with a Vycor plug separator and a platinized-platinum wire over which hydrogen gas was bubbled. The working electrode potential scanning rate was 100mV/s unless otherwise stated.

A steady state fuel cell polarization curve was obtained using a custom made cylindrical Teflon cell. Pt-catalyzed Teflon-bound porous gas-fed electrodes (BASF/E-TEK V3 ELAT) were used for both anode and cathode. The Pt loading on these electrodes is  $0.5\text{ mg/cm}^2$ . The geometric working area of the electrodes was  $0.5\text{cm}^2$ ; the liquid layer was 3.0 mm thick, and the real resistance of the 2-FPTf electrolyte was  $8.9\text{ Ohm cm}^2$  at  $80^{\circ}\text{C}$ . Dry hydrogen and oxygen gases were delivered to the anode and cathode at flow rates of 20 sccm and 10 sccm, respectively. A Keithley 2440 source meter interfaced to a computer and a LABVIEW program controlled the cell current, and the cell voltage was recorded when the change in cell voltage was less than 1 millivolt per minute. All curves are reported with no correction for internal resistance.

## Results and Discussion

Figure 1 shows the voltammograms for Pt in aqueous 1M trifluoromethanesulfonic acid (top) and trifluoromethanesulfonic acid monohydrate (bottom) electrolytes equilibrated with 1 atmosphere of dry Argon (dashed line) and oxygen (solid line) gas at  $80^{\circ}\text{C}$ . The voltammograms under Argon are typical of a clean Pt surface in weakly adsorbing aqueous electrolyte with the characteristic symmetrical reductive hydrogen-ion adsorption and oxidative hydrogen-atom desorption currents between 0.35 and 0.05 V versus RHE, asymmetrical Pt-oxide formation starting at about 0.8V vs. RHE on the positive-going potential sweep and Pt-oxide reduction ending at about 0.5V on the negative sweep and finally double-layer capacitive charging in between. The onset of Pt-oxide formation is suppressed in TFMSA-monohydrate, because the water-activity of this electrolyte is much lower than in aqueous 1M TFMSA. At potentials below 1V vs. RHE, the curves were not symmetrical about the x-axis, as is expected, but were shifted slightly

to negative currents, but this is an artifact due to oxygen reduction from incomplete degassing of air by Argon.

Introducing oxygen to the electrolytes resulted in large negative currents, which started near 1 V vs. RHE and increased in magnitude as potentials were scanned more negatively. Clearly, the new negative currents were due to oxygen reduction on Pt. Although aqueous 1M triflic acid and TFMSA-mono-hydrate are both considered aqueous electrolytes, the TFMSA-mono-hydrate is essentially a pIL which is formed by transfer of proton from the acid, TFMSA, to the base, water, to give the “salt”, TFMSA-mono-hydrate. In TFMSA-mono-hydrate electrolyte, Pt-oxide formation is more difficult and occurs at higher potentials than in aqueous 1M triflic acid, and subsequently the Pt is metallic and the onset of oxygen reduction occurs at higher potentials (just above 1V vs. RHE). Why? In TFMSA-mono-hydrate, the water in this “salt” electrolyte is not reactive “bulk-like water” but has limited reactivity, because the water is bound by the stabilization energy of salt formation. Water can not react with Pt to form Pt-oxide until this stabilization energy is provided to separate water from TFMSA, which amounts to an overpotential (shift to higher positive potentials) for Pt-oxide formation. This allows Pt to be in the metallic state at higher potentials. The diffusion limiting current for oxygen reduction (at  $\sim 0.1$  V vs. RHE) was higher for TFMSA-mono-hydrate ( $-3.5$  mA/cm<sup>2</sup>) than the dilute 1 M triflic acid solution ( $-0.5$  mA/cm<sup>2</sup>). This difference is probably due to a higher oxygen concentration in TFMSA-mono-hydrate, since TFMSA-mono-hydrate has higher fluorocarbon content, and fluorocarbons are known to have higher oxygen solubility than water. Aqueous 6M TFMSA is a concentrated aqueous electrolyte. The features in the voltammogram of Pt in aqueous 6M triflic acid (not shown) are similar to TFMSA-mono-hydrate but are intermediate to that for aqueous 1M TFMSA and TFMSA-mono-hydrate, essentially because aqueous 6M TFMSA has intermediate free water-activity.

Figure 2 shows the voltammograms of Pt in a neat 2-FPTf salt electrolyte equilibrated with 1 atmosphere of argon and oxygen gas at 80°C, which were stable for many hours at 80°C. The voltammogram of Pt in 2-FPTf is similar to that for TFMSA-mono-hydrate under oxygen (Fig. 1). Still there is reductive proton adsorption and oxidative hydrogen atom desorption. However careful inspection of Figures 1 (for TFMSA-mono-hydrate) and 2 (for 2-FPTf) show that oxygen reduction on Pt in the truly non-aqueous 2-FPTf electrolyte starts nearer the thermodynamic limit (1.2 V vs. RHE) than in TFMSA-mono-hydrate. Also the oxidation currents above 1.2V are not for Pt-oxide formation but apparently are for oxidation of water to oxygen, as will be discussed later [5]. Voltammetry of Pt in 2-FPTf electrolyte was performed at higher temperatures, and a Pt voltammogram at 120°C (not shown) indicated the 2-FPTf electrolyte slowly decomposed in the presence of Pt at temperatures near 120°C and above [4].

Fig. 3 shows the steady state polarization curves for a fuel cell fed dry hydrogen and oxygen at ambient pressure in neat 2-FPTf, aqueous 85% phosphoric acid and aqueous 6M triflic acid at 80°C and neat 2-FPTf 120°C. Aqueous 6M triflic acid was used instead of TFMSA-mono-hydrate, because the latter wets Teflon severely.

The polarization curve for 2-FPTf at 80°C showed a 0.1 V voltage gain over all current densities (less polarization) compared to that with aqueous 85% phosphoric acid electrolyte.

The polarization curve at 80°C for 2-FPTf was almost - but not quite - as good as that for aqueous 6M triflic acid. At lower current densities ( $<5 \text{ mA/cm}^2$ ) the fuel cell with 2-FPTf electrolyte showed 25 mV lower cell voltage (more polarization) than with 6M triflic acid as the electrolyte, and at high current densities, e.g., at  $\sim 100 \text{ mA/cm}^2$ , there was 0.35V higher cell voltage with 6M TFMSA versus with 2-FPTf. Even though performance with 2-FPTf was not quite as good as TFMSA-monohydrate, the result with 2-FPTf is still quite remarkable, since triflic acid is considered one of the best acid electrolytes to use for Pt-catalyzed oxygen electroreduction and hydrogen electrooxidation [6].

Continued fuel cell operation at 80°C showed the fuel cell with 2-FPTf remained stable for many hours, whereas the cell with 6M triflic acid gradually dropped in performance. Water is slowly lost from the aqueous 6M triflic acid electrolyte in a fuel cell fed dry gases, and the 6M triflic acid dehydrates to TFMSA-monohydrate under the dry  $\text{H}_2$  and  $\text{O}_2$  feed-gas streams. The gradual loss of performance in the fuel cell with aqueous 6M TFMSA results, because aqueous triflic acids that are more concentrated than 6M wet and flood the Teflon bound electrodes, choking off the  $\text{H}_2$  and  $\text{O}_2$  gas supplies in the fuel cell which leads to severe concentration polarization.

Although 2-FPTf was stable under fuel cell operating conditions at 80°C for an extended time (days), at 120°C the polarization curve for 2-FPTf degraded significantly compared to the polarization curve for 2-FPTf at 80°C. This apparently was due to the decomposition of 2-FPTf at 120°C which subsequently poisons the Pt catalyst. After fuel cell operation at 120°C, the 2-FPTf electrolyte became dark in color. A similar darkening of the electrolyte and loss of oxygen reduction activity was observed in the voltammogram of Pt in 2-FPTf at 120°C (not shown). The most likely reason for the decomposition is Pt-catalyzed oxidation of the “activated” carbon-hydrogen bond adjacent to the nitrogen in the 6 position of the pyridine ring in the presence of oxygen. New more highly fluorinated pILs, including 2,6-difluoropyridinium triflate, are being prepared in an attempt to extend the stable operating temperature of a pIL electrolyte to 120°C.

## Conclusions

Fluorocarbon protic salt electrolytes are promising as non-aqueous proton conducting electrolytes for a fuel cell, due to their enhanced stability when reactive CH bonds are replaced by inert CF bonds. A Pt-catalyzed  $\text{H}_2/\text{O}_2$  fuel cell with a new fluorinated pIL electrolyte, 2-fluoropyridinium triflate (2-FPTf), showed higher performance than one with aqueous 85% phosphoric acid electrolyte at 80°C. The higher performance is attributed to decreased polarization for oxygen reduction on Pt in 2-FPTf, because Pt is metallic at high potential due to the low activity of “bulk-like” water in the 2-FPTf

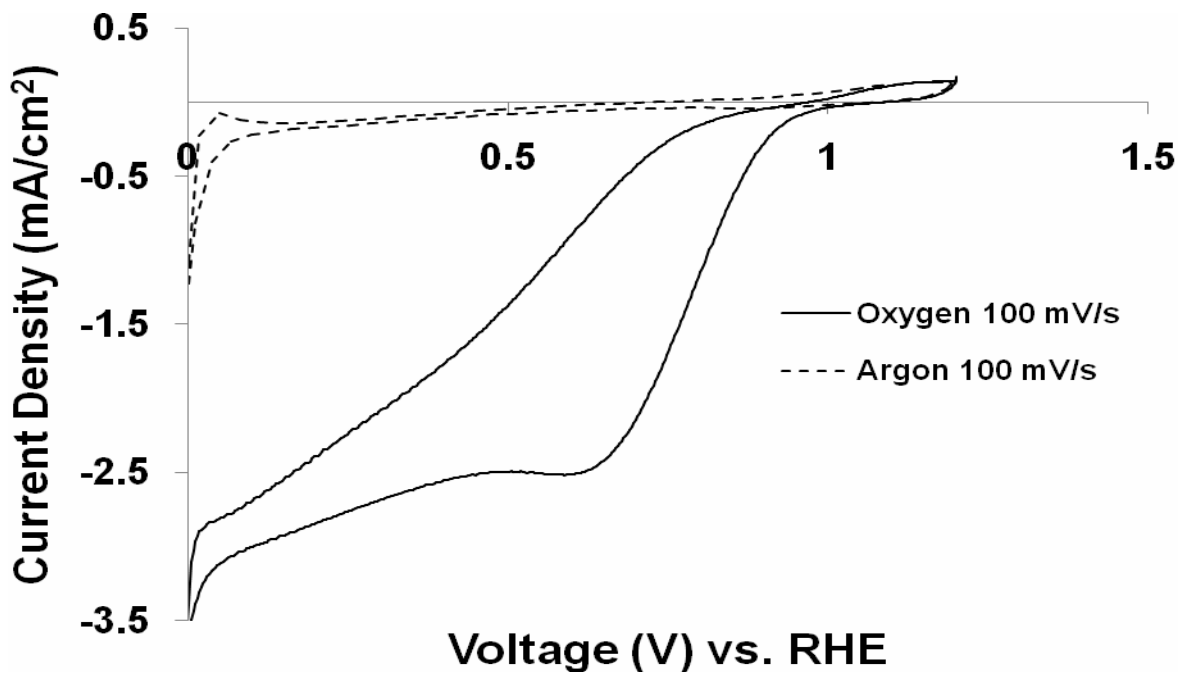
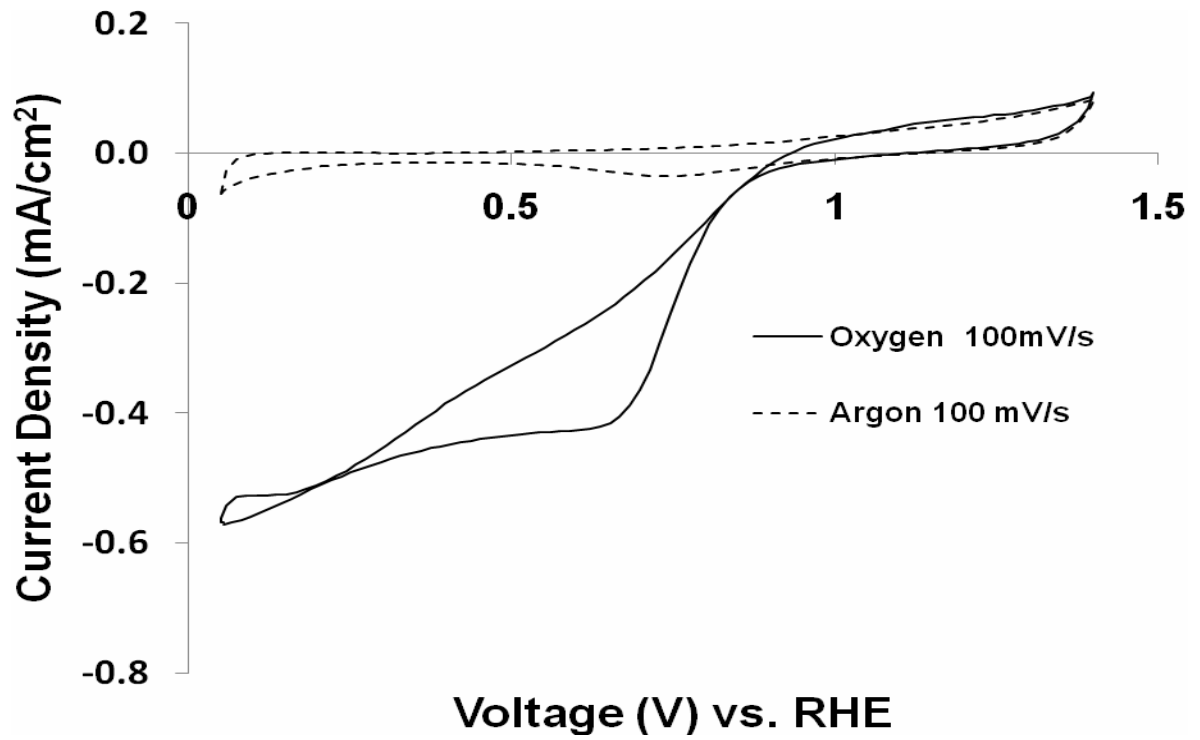
electrolyte. At 120°C, the 2-FPTf decomposed, so work is in progress to further substitute fluorine for hydrogen in the reactive carbon-hydrogen bonds (e.g., the other H adjacent to N in 2-FPTf) in the pIL electrolyte, in order to further improve electrolyte stability and fuel cell operating life. These pIL electrolytes are considered as models for choosing the ionic constituents in protic salt polymers for forming new proton-conducting solid polymer electrolyte membranes for use in fuel cells with operating temperatures ranging from below freezing to over 120°C.

### Acknowledgement

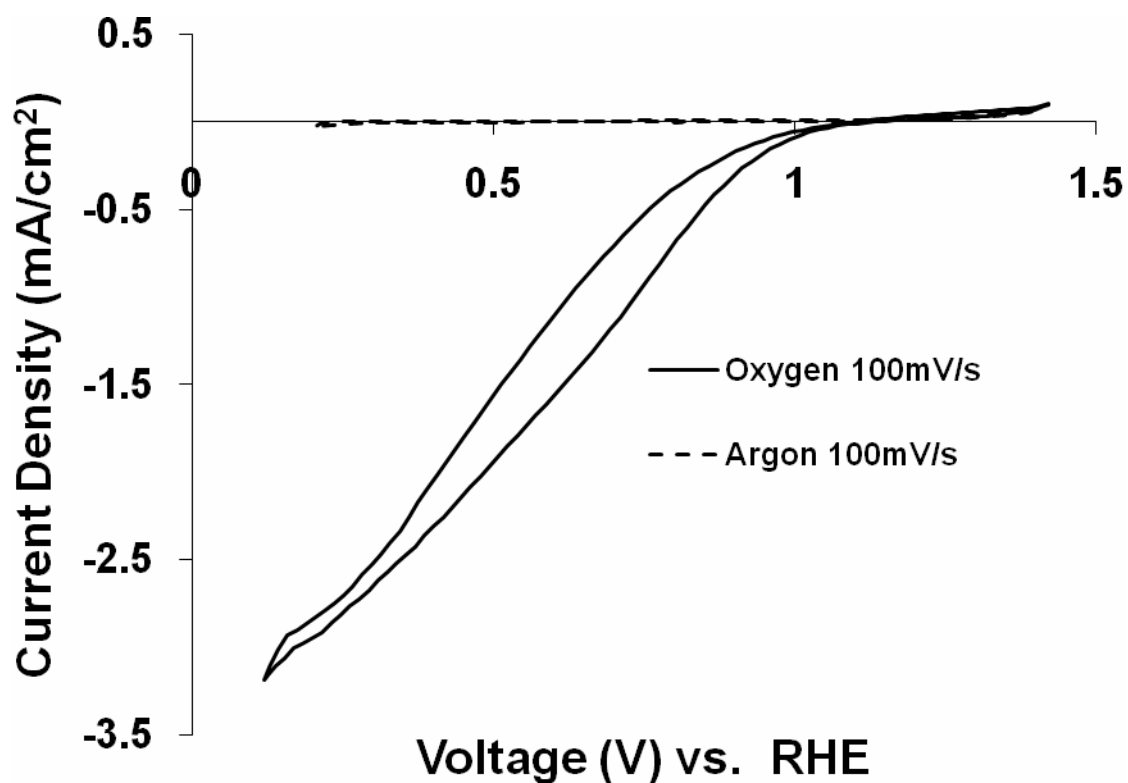
The authors gratefully acknowledge support of the Department of Energy, DoE Project Number DE-FG36-06G016029; Reginald Tyler, DoE Manager; and Terry Payne, DoE Technology Development Officer.

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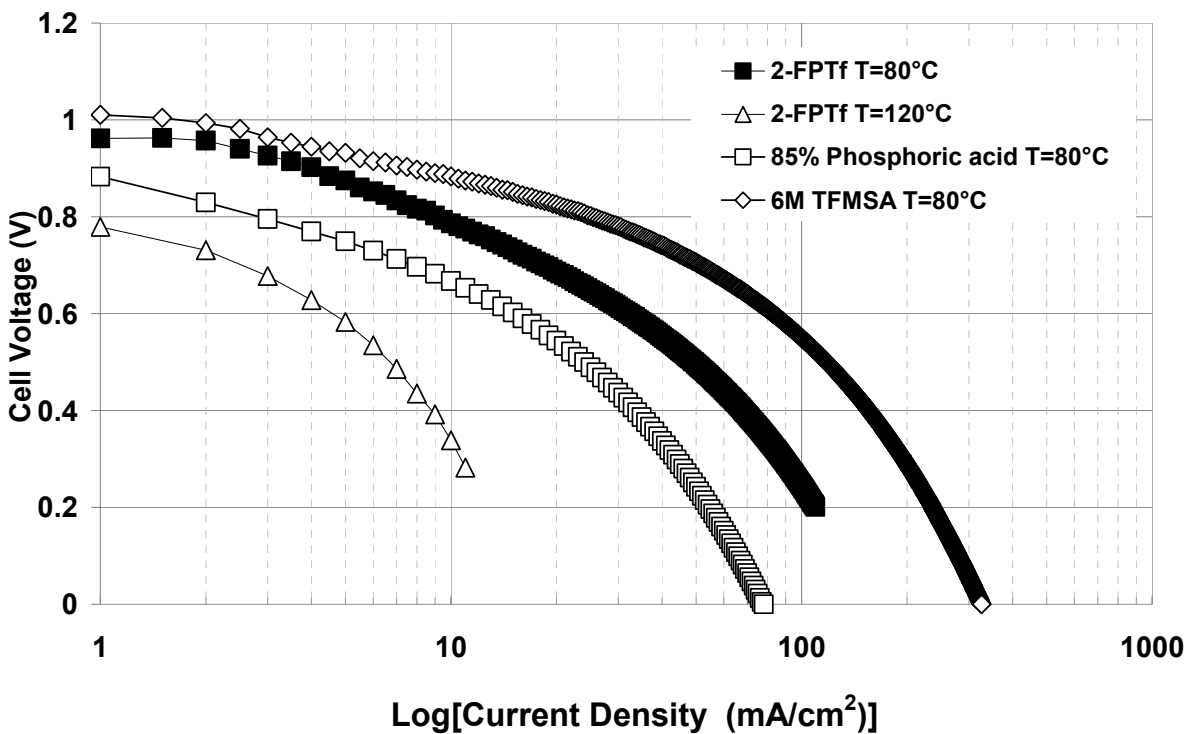
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**Figure 1.** Voltammetry of Pt in aqueous 1M trifluoromethane sulfonic acid (top) and triflic acid monohydrate (bottom) at 80°C under Ar (dashed line) and O<sub>2</sub> (solid line). P<sub>gas</sub> = 1 atm. Scan Rate = 100mV/s. Electrode area = 0.1 cm<sup>2</sup>.



**Figure. 2** Voltammetry of Pt in neat 2-fluoropyridinium triflate (2-FPTf) at 80°C under dry oxygen and Argon at a total gas pressure of 1 atm. Scan Rate = 100mV/s. Electrode area = 0.1 cm<sup>2</sup>.



**Figure. 3** Comparison polarization curves for fuel cell fed dry hydrogen and dry oxygen gas with various electrolytes: neat 2-fluoropyridinum triflate (solid square), aqueous 85% phosphoric acid (open square) and 6M triflic acid (open diamond) at 80°C and 2-FPTf at 120°C (open triangle). Pt loading 0.5 mg/cm<sup>2</sup>. Note: these curves are not IR corrected.