Abstract #297, 224th ECS Meeting, © 2013 The Electrochemical Society

Electrokinetic studies of iron-ligand complexes for an all-iron redox flow battery application

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As the energy focus shifts from fossil fuels to renewable sources and smart-grid technology, energy storage becomes a main requirement. Redox flow battery (RFB) technology has seen renewed interest for such a purpose in recent years [1, 2]. Several chemistries for flow batteries exist, such as all-vanadium, iron-chrome, and bromine-polysulfide [3]. One such technology is the all-iron hybrid RFB [4]. This chemistry involves plating iron from Fe(II) on the negative electrode, and the Fe II/III reaction on the positive electrode, for a nominal cell voltage of 1.2 V. Because the negative reaction occurs at -0.44 V vs. NHE, H_2 evolution becomes a significant challenge, which can be mitigated by raising the electrolyte pH above 3. This change in pH, however, presents a problem on the positive side of the battery as iron(III) quickly precipitates as $Fe(OH)_3$ at pHs greater than 2 [5]. This precipitation can be prevented through the use of complexing ligands within the electrolyte.

Several ligands were examined for their stabilizing effect on Fe(III), specifically polyols and carboxylic acids. The ligand must be able to retain a high concentration of Fe(III) in a pH 3 solution without effecting the iron II/III redox kinetics, and without being electrochemically active itself. Several ligands met the initial requirements, including glycerol, glycine, DMSO, and malic acid (Table 1). In a 3:1 ligand to iron(III) ratio in solution, precipitation of $Fe(OH)_3$ was not seen until pHs above 4 for these ligands. Additionally, the reaction potential for the iron II/III-ligand redox couples did not shift significantly. Promising ligands were further investigated for kinetic and mass transfer limitations. Glycerol was found to stabilize iron ions without significant effect to the iron II/III kinetics (Figure 1). This was maintained as the pH of the iron-glycerol electrolyte was raised (Figure 2). At low concentrations of glycerol (0.3 M in Figure 1), the peak height shows very little change from the iron only voltammetry. When the glycerol concentration is increased (2 M in Figure 2), the solution becomes more viscous and the diffusion of the iron-glycerol complex is slowed. The kinematic viscosity of 2 M glycerol in water is 0.014 cm^2/s at room temperature (water is 0.01 cm^2/s) [6]. From the limiting current data (Figure 3), it can be seen that the iron-glycerol limiting current is 82% of the iron II/III limiting current at a rotation rate of 1000 rpm. The iron-DMSO and iron-glycine limiting currents were closer to that of the iron only experiments. In the interest of using a single electrolyte composition, the effects of the ligands on iron plating will also be presented.

References

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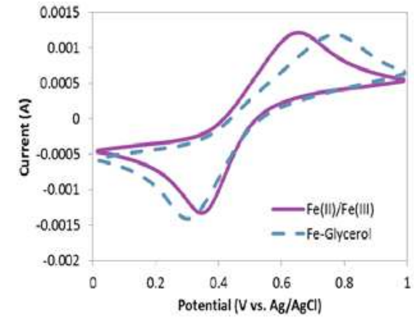

Figure 1. Cyclic voltammetry on a glassy carbon electrode of the Fe II/III reaction with and without the presence of glycerol. Performed in 0.1 M ferrous chloride, 0.1 M ferric chloride, and 1 M sodium chloride electrolyte. Glycerol concentration was 0.3 M.

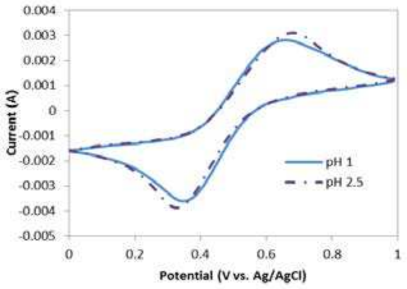

Figure 2. Cyclic voltammetry of the iron-glycerol ligand system on a glassy carbon electrode, at pH 1 and 2.5. Electrolyte for this experiment was 0.5 M ferrous chloride, 0.5 M ferric chloride, 2 M glycerol, and 1 M sodium chloride. The pH was adjusted using sodium hydroxide.

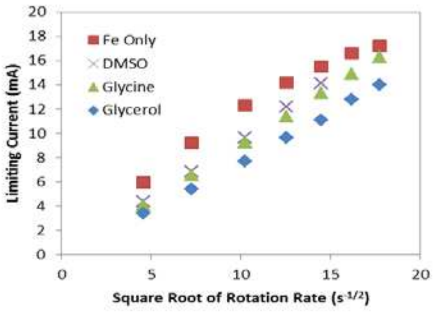

Figure 3. Levich plots for the iron II/III-Ligand redox couples, as compared to the ligand free system. Electrolyte for this experiment was 0.2 M ferrous chloride, 0.2 M ferric chloride, 2 M Ligand, and 1 M sodium chloride. Experiments were performed using a glassy carbon rotating disk electrode.

Table 1. Properties of Selected Ligands.

Ligand	Ligand Solubility (M)	E_o (V vs. NHE)	3:1 pH limit
DMSO	Miscible	0.712	5.66
Glycerol	Miscible	0.659	5.30
Glycine	3.33	0.68	4.64
Malic Acid	4.16	0.711	none

This research is funded by the Department of Energy Office of Electricity, award number 1111358.