

pH Stability and Electrocatalytic Oxygen Evolution Activity of Ferrate

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Ferrate, FeO_4^{2-} is a powerful oxidizing agent with environmentally benign decomposition products. K_2FeO_4 is a reasonably stable form produced by chemical synthesis routes, or electrochemically with reasonable yields $\geq \text{pH } 14$ ¹. Lee et al.² also demonstrated the electrosynthesis of localized ferrate from 6mM FeSO_4 in 0.1M HClO_4 (aq). Ferrate prepared in this manner rapidly oxidizes water at the electrode to form O_2 (g) and cannot be collected as a precipitate.

We utilized a boron-doped diamond (BDD) electrode and 5mM FeSO_4 to further study the nature of ferrate activity and probe for signs of higher oxidation states above Fe(VI). Oxygen evolution begins concurrently with ferrate formation due to the instability of FeO_4^{2-} . Superimposed activity of the two reactions complicates quantitative analysis of electrochemical data. Figure 1 shows a steady decrease in the peak associated with ferrate activity above 1.8V as pH is incrementally decreased from 1 to 0.52. Fe(II)/Fe(III) redox peaks appear unaffected by the pH change. This is verified with differential pulse polarography (inset) which probes initial surface activity before a matured diffusion gradient at the electrode is established. Ferrate activity (Fe(VI) formation with OER) above 1.5V is unaffected by ΔpH until 1.77V, where a higher current is observed in 0.3M HClO_4 . Above this potential, the kinetics of ferrate activity increase with increasing acidity, while diffusion limitations quickly dampen the overall reaction.

Slow polarization rates reveal slower reactions and better distinguish superimposed peaks. Scans at 1mV/s in 0.1M and 0.3M HClO_4 (Figure 2) reveal distinct features not previously reported, nor apparent at faster scan rates. Peaks labeled (I) indicate the nearly reversible Fe(II)/Fe(III) redox couple. The distinct features of peak (II) indicate relative changes in the kinetics of individual steps in ferrate formation and water oxidation as pH is decreased. We will present rotating electrode and potential pulse techniques to distinguish contributions from O_2 saturation, electrode OER, and further Fe activity within peak (III) as pH decreases.

The stability of Fe(2)/Fe(3) yields linear I_p vs. $\text{Time}^{1/2}$ behavior in Figure 3(A). Assuming a charge transfer of $1e^-$, the estimated diffusion coefficient of this couple is $1.2\text{--}1.3\text{E-}6 \text{ cm}^2/\text{s}$. Figure 3(B) shows the same analysis of what is presumably the Fe(III)/Fe(VI) couple ($n=3e^-$ assumed, without charge transfer from OER). The concentration of Fe(III) remains high near the electrode due to the rapid reduction of Fe(VI), resulting in an overestimation of the diffusion coefficient, $1.6\text{E-}4 \text{ cm}^2/\text{s}$. These values are very similar to estimates obtained using the Cottrell equation from chronoamperometric analysis at each peak potential (not shown).

We are currently identifying these key parameters to enable further kinetic and mechanistic analysis. These results will be complimented by electrochemical analysis and characterization (XPS, XRD, TGA) of ferrate produced through various means under basic conditions.

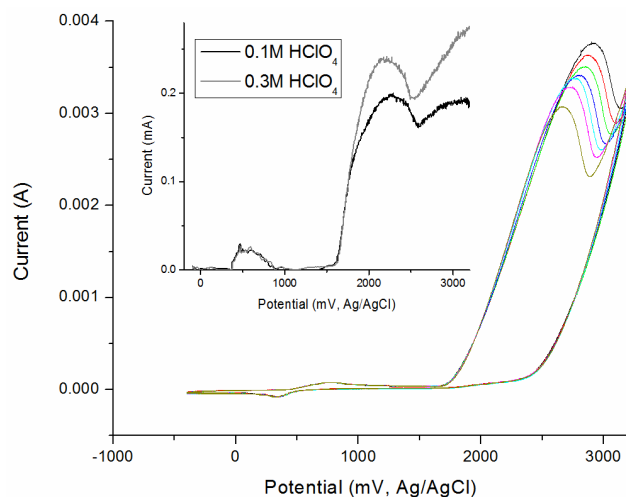


Figure 1: Cyclic voltammetry at 30mV/s of 5mM FeSO_4 in 0.1M (black) to 0.3M (yellow) HClO_4 (33mM increases). Inset: Differential pulse polarography across the same potential range.

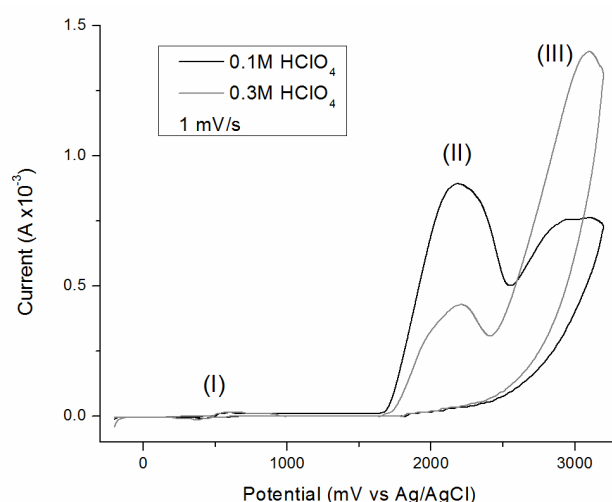


Figure 2: Cyclic voltammetry of 5mM FeSO_4 at 1mV/s, revealing Fe(II)/Fe(III) (I), and Fe(III)/Fe(VI) with OER (II). O_2 saturation, BDD and Fe activity contribute to (III).

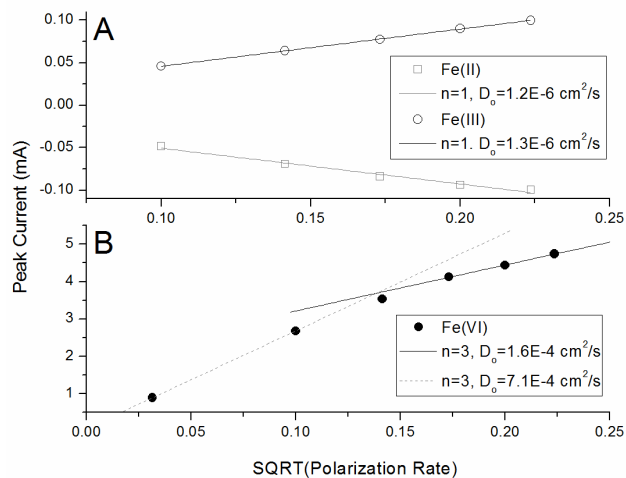


Figure 3: I_p vs $v^{1/2}$ dependence of Fe(II) and Fe(III) (A) and Fe(VI) peaks (B). Electron transfer values, n , were used to estimate the diffusion coefficient of each reactant.

References:

- Máková, Z., K. Bouzek, J. Híveš, V.K. Sharma, R.J. Terryn, J.C. Baum, *Electrochimica Acta*, 54(10), 2673-2683, (2009)
- Lee, J., D.A. Tryk, A. Fujishima, S. Park, *Chemical Communications*, (5), 486-487, (2002)