

Optimisation of an Iron Redox Flow Cell Cathode

J. Swaine

January 19, 2025

Abstract

Batteries are ubiquitous in everyday life and finding ways to improve their performance is imperative. The iron redox flow cell has been proposed as a cheap and safe energy storage solution but poses notoriously slow kinetics at the anode and cathode. This study focuses on optimising the cathode via variation of electrolyte cation and pH for a 1mM hydrated iron (II) sulphate system. Initially, 0.1 M electrolyte solutions of Cs_2SO_4 , $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, K_2SO_4 and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ were investigated to identify the optimal cation for the system, with selection based on the highest peak current magnitudes observed in cyclic voltammetry. Selecting the electrolyte that corresponded to the greatest peak magnitudes, the pH of the system was varied within the acidic region, and its influence on the electrochemical performance was analysed. Results indicated that potassium sulphate offered the best performance of the electrolyte set, and saw maximum peak currents of $i_p^{ox} = 9.01 \mu\text{A}$ and $i_p^{red} = 6.04 \mu\text{A}$ at a pH of 3.46. The results suggest that the electrochemical system performs best with what is a slightly larger cation species and that this is further improved by acidic conditions. In further investigation rubidium sulphate may be considered as an electrolyte species candidate and a greater number of pH regions may be investigated.

1 Method

Four separate 50 ml, 0.1M solutions of Cs_2SO_4 (1.809 g, 0.005 mol), $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (0.635 g, 0.005 mol), K_2SO_4 (0.871 g, 0.005 mol) and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (1.612 g, 0.005 mol) were made up in deionised water. Four 25 ml 1mM solutions of hydrated iron (II) sulphate were then made via dissolution of hydrated iron (II) sulphate (0.007 g, 2.5×10^{-5} mol) in each of the electrolyte solutions. Samples of each solution were taken and placed in an electrochemical cell. A working carbon electrode, reference stainless steel electrode and reference Ag/AgCl electrode were placed in the cell and connected to the potentiostat. PStrace software was employed in conjunction with the potentiostat to perform measurements to generate the cyclic voltammograms. The following settings were used: $E_{begin} = 0 \text{ V}$, $E_{vertex1} = 0.6 \text{ V}$, $E_{vertex2} = 0 \text{ V}$, $t_{equilibration} = 10 \text{ s}$, $E_{step} = 0.01 \text{ V}$ and no. of scans = 1. Scans were recorded at scan rates of 0.01 V s^{-1} , 0.02 V s^{-1} , 0.05 V s^{-1} , 0.1 V s^{-1} , 0.2 V s^{-1} and 0.5 V s^{-1} . Once all cyclic voltammograms had been obtained, a best electrolyte was identified on the basis of having the largest oxidation and reduction peak magnitudes. K_2SO_4 electrolyte was selected and a new 25 ml, 1mM solution of hydrated iron (II) sulphate was made in the same way as before.

This solution was then separate into four different samples. To each sample was added varying amounts of 0.05 M sulphuric acid, generate the following pH values: 5.97, 4.29, 3.46 and 2.03. Cyclic voltammograms were taken for each measurement and results were collated and tabulated to again identify the system with the greatest peak magnitudes.

2 Results and Discussion

2.1 Variation of the Electrolyte

Changing the cation within the electrolyte, maintaining a consistent electrolyte concentration of 0.1 M, was seen to effect the character of the obtained CV. Figure 1 displays the CVs of Hydrated Iron (II) Sulphate within various electrolyte soltuions, with the "best" (most reversible one) emphasised in bold black – the potassium sulphate electrolyte.

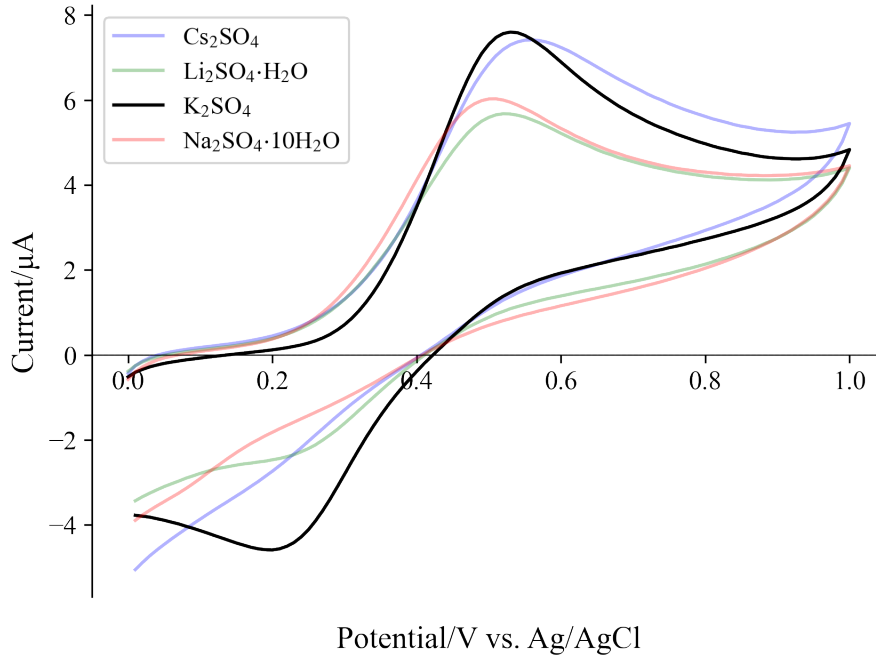


Figure 1: Cyclic Voltammogram of 1 mM Hydrated Iron (II) Sulphate in various electrolyte at 0.1 M, with a scan rate of 0.1 Vs⁻¹.

In the case of Potassium Sulphate, a strong forward peak is noted at $E_{ox} = 0.53$ V with an associated peak current of $i_p^{ox} = 6.49$ μA. A reduction peak is noted at $E_{ox} = 0.20$ V with a reduction peak magnitude of $i_p^{red} = 3.16$ μA. It is evident we have not observed a fully electrochemically reversible reaction as $|i_p^{ox}| \neq |i_p^{red}|$, and $\Delta E = 0.33$, however, the potassium sulphate system clearly possesses the most reversible character and as such can be classified as the "best". This classification is subjective, but in this case it is judged with respect to the systems ability to mimic the charge and discharge that would be expected within a functioning electrochemically reversible energy storage cell.

2.2 Variation of the pH

By visual inspection of Figure 2 and quantification through table 1, pH 3.46 shows the highest oxidation and reduction peak magnitudes, as well as a reasonable value for ΔE . The interdependency of current and diffusion coefficient is well known and so we can recognise that a greater peak current magnitude corresponds to a larger diffusion coefficient, D , which implies that the potassium sulphate electrolyte exhibits the greatest D value, and that a pH in the region of 3.5 will increase it further.

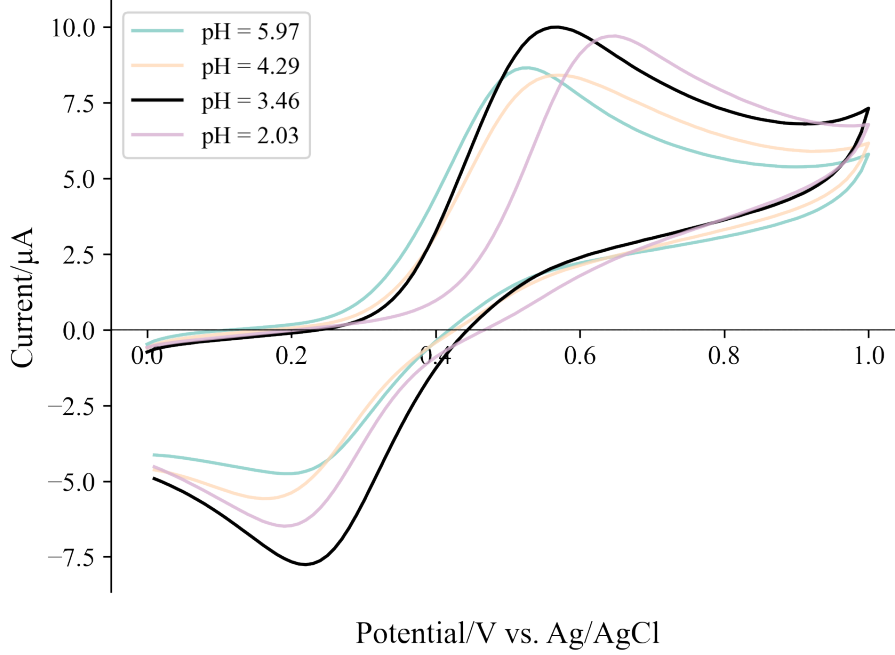


Figure 2: Cyclic Voltammogram of 1 mM Hydrated Iron (II) Sulphate in Potassium Sulphate electrolyte at 0.1 M, at varying pH, with a scan rate of 0.1 Vs^{-1} .

Table 1: Tabulation of peak current in a pH varied Hydrated Iron (II) Sulphate redox system, at 298K.

pH	$ i_p^{ox} $ (μA)	$ i_p^{red} $ (μA)	E_{eq} (V)	ΔE (V)
2.03	8.51	4.50	0.42	0.46
3.46	9.01	6.04	0.40	0.35
4.29	7.42	3.31	0.37	0.41
5.97	7.77	2.76	0.36	0.34

Table 1 verifies that $\text{pH} = 3.46$ provides the largest oxidation and reduction peak magnitudes. This can be rationalised in different ways, but let us initially consider Marcus Theory. Electron transfer will not occur until certain conditions have been met. Both species must have the same nuclear geometry and hence, be isoenergetic to one another, resulting in the donor HOMO and recipient LUMO being equal in energy. It is clear that there will be an energetic cost to achieving these conditions, this cost takes

the form of the activation energy, ΔG^\ddagger . Activation energy is dependent on free energy, ΔG° , and reorganisation energy λ . A smaller ΔG^\ddagger implies a larger value for k° , and as given by the Butler-Volmer equation, will result in a larger current value, i . The opposite will hold true for iron (II) sulphate. It is unlikely that difference in system free energy will be large, as all experiments were conducted at ambient room temperature, so the difference can mainly be attributed to λ . Proton coupled electron transfer (PCET) may also be considered. Detailed in Saouma et al. (2015)¹, PCET is well observed in Fe-S clusters and as such it would be reasonable to suggest that this might occur in this instance too, however, this cannot be verified and would need more investigation. Overall, whilst electrolyte composition (with respect to a discrete selection of cations) has been optimised, a limited sample set of pH environments only provides an idea of where a "perfect" pH might lie rather than actually providing the value itself and so requires further investigation.

3 Conclusion

The results show that for a 1mM hydrated iron (II) sulphate system, a 0.1 M K_2SO_4 electrolyte is optimal with respect to our considered discrete set. It is clear that this system also sees improvement in the acidic region around $pH \approx 3.5$, noting maximum peak values at $i_p^{ox} = 9.01 \mu A$ and $i_p^{red} = 6.04 \mu A$. It is however, clear that this does not represent a fully electrochemically reversible system as $\Delta E = 0.35$. Future investigations could explore the potential of rubidium sulphate as an alternative electrolyte or investigate the effects of substituting the sulphate anion while maintaining potassium as the cation. Additionally, finer control over system acidification could be investigated by using an adjustable micropipette to introduce specific sulphuric acid volumes to a standard solution, enabling a more precise range of acid measurements, allowing better deduction of optimal pH for the system.

References

- [1] C. Saouma, W. Morris and J. Darcy, *National Library of Medicine*, 2015, **25**, 9256–9260.