Influence of Mixed Electrolyte on the Performance of Iron-Ion/Hydrogen Redox Flow Battery

Venroy Watson,∗ Derrick Nguyen,† Edward E. Effiong,‡ and Egwu E. Kalu∗,†,‡

∗Department of Chemical & Biomedical Engineering, Florida A&M University, Tallahassee, Florida 32310, USA
†Department of Environmental Engineering, University of Oklahoma, Norman, Oklahoma 73019, USA
‡Department of Chemical Engineering, Federal University of Technology, Owerri, Nigeria

Improved chargedischarge performance of Iron-ion/Hydrogen redox flow battery (RFB) electrolyte with a mixed FeSO4 and FeCl2 is reported. Addition of Cl− ions into a sulfate electrolyte changes the charge/discharge behavior of the sulfate electrolyte leading to a reduction in charging potential for a mixed FeSO4 and FeCl2 electrolyte system. This suggests that a sulfate/chloride electrolyte system can lead to improved charge/discharge of the Fe-ion/H2 RFB. Reverse addition of FeSO4 to FeCl2 showed a decrease in the mixed electrode transfer efficiency (experimental current relative to theoretical) equivalent to a decrease in electrolyte performance. We deduce that 0.8 M FeCl2 corrosive electrolyte can be replaced by less corrosive mixture of 46 mol % Cl− in 0.8 M FeSO4 to achieve the same performance that can be obtained using an all chloride system.

© The Author(s) 2015. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0091507eel] All rights reserved.

Materials and Methods

An equimolar 0.8 M amounts of FeSO4 and FeCl2 and their acids (H2SO4 and HCl, respectively) were mixed and degassed with N2 for one hour. Pt, graphite and glassy carbon working electrodes were used along with Pt wire counter electrode and Ag/AgCl reference electrodes in both divided and undivided cell set-up. In the divided cell set-up, Nafion 212 membrane was used as the separator. In both set-ups, linear scanning voltammetry (LSV) and cyclic voltammetry (CV) analysis were carried out using a Gamry Instruments Interface 1000 potentiostat/galvanostat/ZRA. Scan rates varied from 0.025 to 0.01 V/s. For simple H-cell charge/discharge arrangements, both Pt catalyzed carbon cloth and Pt foil working electrodes were evaluated for preliminary and worst case performances without system optimization.

Results and Discussion

The balanced electrochemical reactions of iron-ion/hydrogen ion RFB during discharge are:

Cathode:

$$Fe^{3+}_{\text{aq}} + e^- \rightarrow Fe^{2+}_{\text{aq}} \quad E_w = 0.77 \text{ V vs. SHE} \quad [2]$$

Anode:

$$\frac{1}{2} H_2 \rightarrow H^+ + e^- \quad E_w = 0.00 \text{ V vs. SHE} \quad [3]$$

∗Electrochemical Society Active Member.
†E-mail: ekalu@eng.fau.edu

Downloaded on 2018-07-21 to IP 207.241.231.80 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
As expected, iron chloride exhibited higher peak currents during the redox process, presumably due to the higher charge carrying capacity of the chloride ions (0.00027 cm²/Vs). Tucker et al. proposed that the two best electrolytes for iron-ion/hydrogen ion RFB are iron chloride and iron sulfate. However, chloride is corrosive and will increase cost of materials used in the battery fabrication. To capture the excellent properties of both chloride and sulfate electrolytes, we hypothesized that a mixture of both electrolytes in various volume ratios could yield a better working electrode. In addition, hydrogen evolution competes with the Fe³⁺ reduction, however hydrogen overvoltage is much higher in graphite than in Pt and thus graphite is more favorable for the iron electrode material for further use in Fe²⁺/Fe³⁺ redox reaction studies.

A systematic addition of 0.8 M FeCl₂ into 0.8 M FeSO₄ was carried out and the results are shown in Fig. 2. Both Figures 2a and 2b show increasing electron transfer efficiency (81% to 96%) as the chloride addition goes from 1 – 50% (V/V) 0.8M iron sulfate. The result clearly indicates that chloride addition to sulfate electrolyte enhances the peak currents of the redox reaction, while exhibiting reversibility over the same voltage range of 0.68V and 0.3 V for the oxidation and reduction peaks, respectively on graphite WE. A similar observation was made when GC and platinum electrodes were used as the working electrodes.

To better understand the influence of chloride addition into sulfate electrolyte, the actual electrons transferred (assuming Eq. 2 reaction occurs) is calculated using Randles-Sevcik equation and this is compared to the theoretical number of electrons (Eq. 1), for electrode efficiency or electrolyte performance. The electrolyte ‘performance’ as used here, compares the theoretical charge transfer or current flow versus the measured current flow on a particular electrode. For instance in a 100% Fe (II) sulfate electrolyte, the theoretical current flow for one electron transfer using Randles-Sevcik equation is compared to experimentally measured current to determine the electron transfer efficiency as approximately equal to 68%.

Overall reaction:

\[
Fe^{3+} + \frac{1}{2} H_2 \rightarrow Fe^{2+} + H^+ \quad E_{o} = 0.77 \text{ V vs. SHE} \quad [4]
\]

As seen in Eqs. 2 and 3, a single electron exchange is involved in the battery’s discharge or charge. A simple CV technique utilized in the analysis of Fe³⁺ containing solution results in the characteristic reversible redox duck-like curves shown in Fig. 1a. Graphite electrode was used as working electrodes for both curves whose anodic peak currents are 0.016A and 0.028A for the sulfate and chloride solutions, respectively. Both anodic peaks occurred at approximately 0.68V which is representative of the Fe²⁺ to Fe³⁺ in both electrolytes. As expected, iron chloride exhibited higher peak currents during the redox process, presumably due to the higher charge carrying capacity of the chloride ions (0.00052 cm²/Vs) compared to the sulfate ions (0.00027 cm²/Vs). Tucker et al. proposed that the two best electrolytes for iron-ion/hydrogen ion RFB are iron chloride and iron sulfate. However, chloride is corrosive and will increase cost of materials used in the battery fabrication. To capture the excellent properties of both chloride and sulfate electrolytes, we hypothesized that a mixture of both electrolytes in various volume ratios could yield a better performance as used here, compares the theoretical charge transfer or current flow versus the measured current flow on a particular electrode.
efficiency increased from about 66% to 92%. This clearly confirms that chloride addition to sulfite electrolyte plays a significant role in enhancing the electrolyte’s charge/discharge performance as shown in Fig. 1b CV where increased peak current was obtained after mixing chloride and sulfite electrolytes. Results in Fig. 2b further suggest that a mixture of chloride and sulfite can perform even better than chloride alone. For instance, based on Fig. 2b results, the addition of 46 mol % chloride ion into 56 mol % sulfite electrolyte results in equivalent electrolyte performance (electron transfer efficiency) as 100 mol % chloride ion of same concentration. In respect of corrosion, we speculate that a 100% chloride electrolyte is more corrosive than a 100% chloride electrolyte containing 50% chloride and 50% sulfite. This may be due to the higher mobility of 0.00052 cm²/Vs Cl⁻ ions. The work suggests that a mixed sulfate/chloride electrolyte system can lead to an improved charge transport. It can be shown that for the two electrolytes (1 and 2, respectively) at the same charge current, the relationship between the charge voltages (V), transfer efficiencies (η) and electrolyte resistances (rs) is \( V_2 = V_1(\frac{\eta_2}{\eta_1}) \). Since the increase in electron transfer efficiency is attributed to chloride addition, it can also be responsible in reducing the charge voltage due to increase in reversibility of the redox reaction aiding Fe³⁺ to Fe²⁺. This result is very promising and supports the earlier deduction reached through the evaluation of electron transfer efficiency in CV experiments. Thus, both results obtained using simple CV techniques and H-cell charge/discharge setup point to probable validity of a mixed chloride and sulfite electrolyte as better performing electrolyte for iron-ion/hydrogen RFB. Also, the authors are not aware of any existing report in the literature detailing the effect and use of mixed (chloride and sulfite) electrolyte in the iron-ion/hydrogen RFB.

Conclusions

The conclusion of the CV results is in agreement with a full cell study in literature comparing the sulfate and chloride electrolyte performances for iron-ion/hydrogen-ion RFB. The new results from the present study show that the addition of Cl⁻ increases performance of sulfite electrolyte. This may be due to the higher mobility of 0.00052 cm²/Vs Cl⁻ ions. The work suggests that a mixed sulfite/chloride electrolyte system can lead to an improved charging/discharging of the Fe⁺⁺/H₂ RFB. Based on the results, a 100% pure 0.8 M FeCl₂ corrosive electrolyte system can be replaced by less corrosive mixture of 46 mol % Cl⁻ in 0.8 M FeSO₄ to achieve the same performance of an all chloride electrolyte system. A similar increase in the performance of the electrolyte was observed for the addition of chloride to the Fe⁻⁻/H₂ RFB. Based on the results, a 100% pure 0.8 M FeCl₂ corrosive electrolyte system can be replaced by less corrosive mixture of 46 mol % Cl⁻ in 0.8 M FeSO₄ to achieve the same performance of an all chloride electrolyte system. A similar increase in the performance of the electrolyte was observed for the addition of chloride to the Fe⁻⁻/H₂ RFB. Based on the results, a 100% pure 0.8 M FeCl₂ corrosive electrolyte system can be replaced by less corrosive mixture of 46 mol % Cl⁻ in 0.8 M FeSO₄ to achieve the same performance of an all chloride electrolyte system. A similar increase in the performance of the electrolyte was observed for the addition of chloride to the Fe⁻⁻/H₂ RFB. Based on the results, a 100% pure 0.8 M FeCl₂ corrosive electrolyte system can be replaced by less corrosive mixture of 46 mol % Cl⁻ in 0.8 M FeSO₄ to achieve the same performance of an all chloride electrolyte system. A similar increase in the performance of the electrolyte was observed for the addition of chloride to the Fe⁻⁻/H₂ RFB. Based on the results, a 100% pure 0.8 M FeCl₂ corrosive electrolyte system can be replaced by less corrosive mixture of 46 mol % Cl⁻ in 0.8 M FeSO₄ to achieve the same performance of an all chloride electrolyte system. A similar increase in the performance of the electrolyte was observed for the addition of chloride to the Fe⁻⁻/H₂ RFB.
ammonium iron sulfate. Furthermore, optimization could be achieved in mixing other redox couples.

Acknowledgments

This work was supported by ERC Program of the National Science Foundation under Award Number EEC-08212121.

References

1. Z. Weber, M. M. Mench, J. P. Meyers, P. N. Ross, J. T. Gostick, and Q. Liu, J. Appl. Electrochem., 41, 1137 (2011).
2. M. Alon, A. Blum, and E. Peled, J. Power Sources, 240, 417 (2013).
3. K. Fatih, D. P. Wilkinson, F. Moraw, A. Ilicic, and F. Girald, Electrochem. Solid-State Lett., 1, B11 (2008).
4. M. C. Tucker, V. Srinivasan, P. N. Ross, and A. Z. Weber, J. Appl. Electrochem., 43, 637 (2013).
5. M. C. Tucker, K. T. Cho, and A. Z. Weber, J. Power Sources, 245, 691 (2014).
6. J. F. Yeager, R. J. Bennett, and R. D. Allenson, in Proceedings 16th Annual Power Sources Conference, p. 39. PSC Publications Committee, Red Bank, NJ (1962).
7. M. A. Streicher, J. Electrochem. Soc., 103, 208 (1956).
8. B.E. Wilde and J. S. Armijo, Corrosion, 23, 208 (1967).
9. Z. Szkłarska-Smialowska, Corros. Sci., 41, 1743 (1999).
10. B. Zaid, D. Saidi, A. Benzaid, and S. Hadji, Corrosion Science, 50, 1841 (2008).
11. A. Parolo, M.C. Merino, A.E. Coy, R. Arrabal, F. Viejo, and E. Matykina, Corrosion Science, 50, 823 (2008).
12. H. Altun and S. Sen, Materials and Design, 25, 637 (2004).