Preview

Return of the Iron Age

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In this issue of *Joule*, Liu and coworkers present the use of the well-known ferrocyanide complex as an active electrode material for an aqueous organic/organometallic redox flow battery. The ammonium cation was used as counter cation in place of the former-utilized sodium and potassium ions. Interestingly, by this simple cation exchange, remarkable capacity and cycle stability were achieved. A battery system is presented comprising ammonium ferrous hexacyanide and an organo-functionalized viologen compound.

An increasing amount of energy is produced by renewables such as wind, hydro, or solar power to significantly decrease CO_2 emissions derived from the utilization of fossil fuels (i.e., coal, gas). It is expected that by 2040 over 40% of the total global energy will be produced by renewable sources.[1] Due to the nonlinear production possibilities of the renewables, the demand for innovative and "green" energy storage systems is rising continuously as the capacities of conventional energy storage such as hydro power, thermal energy, pressurized air, or flywheel-based systems are strongly limited due to geological or physical limitations.[2] As a result, innovative new storage concepts are currently the focus of research.

Redox-flow batteries (RFBs) represent an alternative approach toward conventional static chemical energy storage systems. This battery concept makes it possible to scale the capacity of the battery independently from the power, which is produced, once the battery has been charged. This unique characteristic is enabled by the construction principle of these electrochemical storage systems: two tanks contain an organic or aqueous solution of redox-active organic or inorganic compounds that exhibit reversible reduction and oxidation processes. The electrolyte solutions are pumped into two half-cells that are separated by a membrane and connected to an electrode each, which enables charging and current collection. The energy stored correlates to the volume of the tanks/amount of electrolyte, whereas the power scales with the size of the electrochemical cell/the cell stacks. Numerous systems have been reported utilizing redox-active metal salts (including the most prominent example, the vanadium RFB), organic compounds, as well as polymeric redox systems as active materials.[3,4]

If this battery concept is considered under ecological points of view, multiple requirements must be met when investigating novel electrode materials. Preferably, new electrolytes feature low toxicity, high solubility, high stability upon cycling, and a low materials price.[5] Additionally, the desired electrolyte materials should be already commercially available or accessible through straightforward synthetic routes, enabling large-scale synthesis of the required compounds. Therefore, electrolytes comprising iron-containing compounds

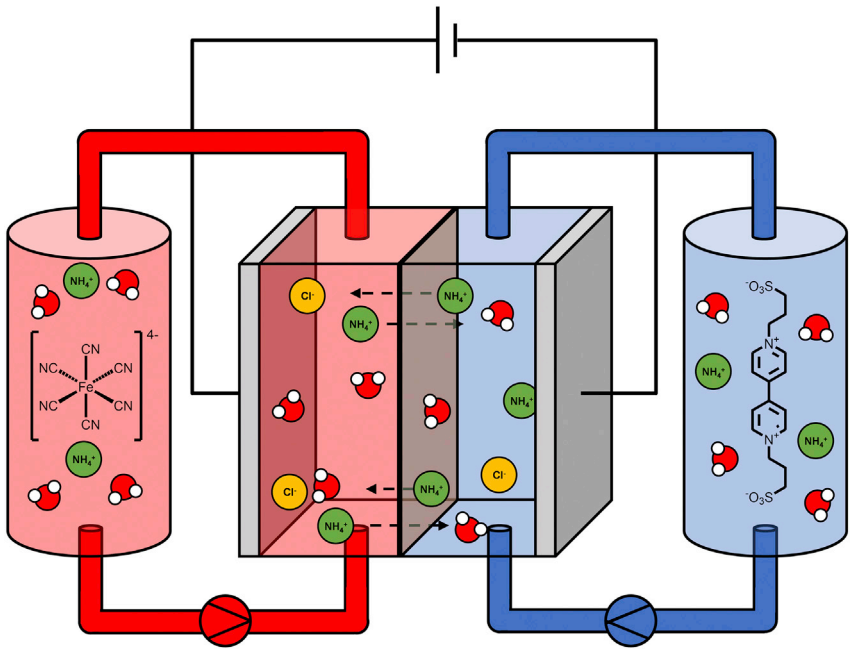


Figure 1. Redox Flow Battery Constructed by Liu and Coworkers

Illustration of the redox flow battery that was reported by Liu and coworkers[10] to investigate the cycle stability of the synthesized ammonium ferrous hexacyanide. The catholyte solution (red) comprises the ferrous hexacyanide salt, and the anolyte solution (blue) contains the bis-sulfonate functionalized viologen.

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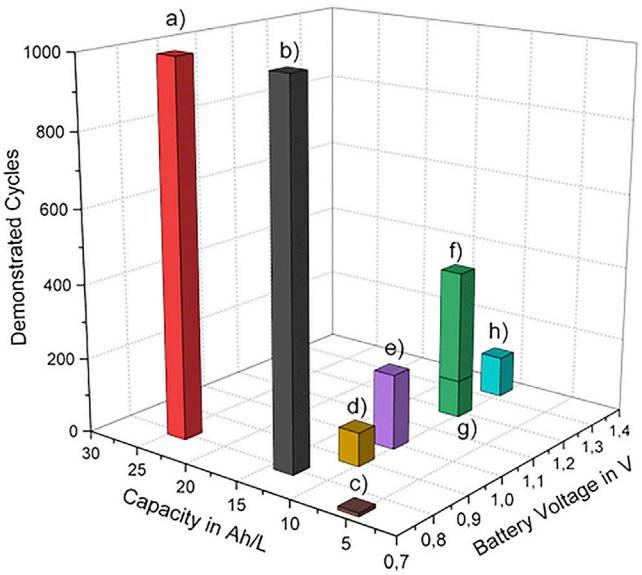


Figure 2. Demonstrated Cycles, Capacity, and Battery Voltage of Comparable Ferrocyanide-Based Redox-Flow-Battery Systems

Illustration of the performed battery cycles, obtained capacity, and battery voltage of different ferrocyanide-based battery systems. Data were obtained from the supplemental information published by Liu and coworkers.[10] 0.9 M $(NH_4)_4[Fe(CN)_6]$ / 0.9 M $(SPr)_2V$ versus 0.9 M $(NH_4)_4[Fe(CN)_6]$ / 0.9 M $(SPr)_2V$ (a); 0.5 M $(NH_4)_4[Fe(CN)_6]$ / 0.5 M $(SPr)_2V$ versus 0.5 M $(NH_4)_4[Fe(CN)_6]$ / 0.5 M $(SPr)_2V$ (b); 0.2 M $K_4[Fe(CN)_6]$ versus 0.1 M anthraquinone-2,7-disulphate (c); excess $K_4[Fe(CN)_6]$ versus 0.2 M naphtoquinone (d); 0.4 M $K_4[Fe(CN)_6]$ versus 0.24 M flavine mononucleotide (e); 0.4 M $K_4[Fe(CN)_6]$ versus 0.5 M alloxazine 7/8-carboxylic acid (f); 0.4 M $K_4[Fe(CN)_6]$ versus 0.5 M 2,6-dihydroxyanthaquinone (g); 0.2 M $Na_4[Fe(CN)_6]$ versus 0.2 M iron-triethanolamine complex (h).

are under investigation, used in both aqueous and non-aqueous media, as the necessary iron salts are inexpensive and many iron complexes can be obtained commercially, even in large scale.[6] For instance, the ferrocyanide and ferricyanide redox pair has been well known and widely investigated in the last 40 years, also with a particular focus on battery applications.[7–9]

The present study focuses on the use of a water-soluble ferrocyanide, namely ammonium ferrocyanide, as catholyte material in a pH neutral flow battery.[10] Through cation exchange a promising electrolyte material was obtained. It features excellent cycle stability and a high solubility in aqueous solution, which eventually results in an increased capacity as well as higher electrolyte conductivity. Compared to $K_4[Fe(CN)_6]$ (0.76 M in water) and $Na_4[Fe(CN)_6]$ (0.56 M in water), $(NH_4)_4[Fe(CN)_6]$ exhibits more than twice the solubility in water and also readily dissolves in 1 M NH_4Cl solution (1.6 M in water and 1.3 M in 1.0 M NH_4Cl). Furthermore, besides the reversible oxidation signal of 0.39 V (versus SHE) for $(NH_4)_3[Fe(CN)_6]$/$(NH_4)_4[Fe(CN)_6]$ in ammonium chloride solution, high conductivities, high diffusion coefficients, and low viscosities were measured, which are necessary preconditions for the desired battery application.

Subsequently, symmetrical cycling experiments revealed excellent stability at a neutral pH value for the $(NH_4)_3[Fe(CN)_6]$/$(NH_4)_4[Fe(CN)_6]$ redox pair in a flow battery setup. The higher solubility of the ammonium salt resulted in a significantly higher initial capacity possible compared to the potassium or sodium salts. After the battery was charged and discharged for 300 consecutive cycles, no significant degradation of electrolyte material or capacity loss was observed.

In the following approach, the $(NH_4)_4[Fe(CN)_6]$ catholyte solution was utilized in an aqueous organic/organometallic redox flow battery (AORFB), paired with a bis-sulfonate functionalized viologen-based anolyte material ($(SPr)_2V$) that was recently published by the Liu group[11] (Figure 1). However, while maintaining high Coulombic efficiency, a total capacity retention of merely 88% was achieved. This significant capacity loss is expected to appear due to significant crossover through the ion exchange membrane and represents a fundamental challenge for the redox flow battery construction. Therefore, the following introduction of "sleeping" electrode material by the authors represents an interesting approach to circumvent the crossover, as osmotic effects may be reduced when the ion strength is identical in both half-cells.

A symmetrical battery test was reported that utilizes a 0.5 M mixture of both $(NH_4)_4[Fe(CN)_6]$ and $(SPr)_2V$ in neutral aqueous ammonium chloride solution on both the anolyte and catholyte sides. As only viologen or ferrocyanide is electrochemically active in the respective half-cell while cycling, the remaining electrolyte material on each side is described as "sleeping." 500 battery cycles were performed with the system, and then the polarization of the electrodes was inverted, revealing the chemical reactivity of the former "sleeping" compounds. In total, the battery was operated for 1,000 cycles, delivering an extraordinary capacity retention of close to 100% per cycle. By extrapolation of the obtained data, a 93.99% capacity retention per year is prospected.

To reach higher theoretical capacities, the active material concentration

was increased to 0.9 M, yielding the AORFB with the highest theoretical capacity (24.1 Ah/L) that has been reported for a ferrocyanide-based system so far (Figure 2). The battery has been cycled for 1,100 h and 1,000 cycles, proving an excellent cycling stability and no significant capacity loss. However, a slightly decreased power and current compared to the 0.5 M solution can be observed, which is ascribed to the increased viscosity as well as the electrolyte and membrane conductivity.

The high stability upon cycling, high initial capacity of the used electrolyte, and hardly any capacity decay even after 1,000 battery cycles make the reported battery system a fascinating and potent candidate for practical applications in energy storage.

DECLARATION OF INTERESTS

U.S.S. and M.D.H. are cofounders of Jenabatteries GmbH. M.D.H. is a shareholder of Jenabatteries.

1. IEA (2018). World Energy Outlook 2018. https://www.iea.org/weo2018/.
2. Yang, Z., Zhang, J., Kintner-Meyer, M.C.W., Lu, X., Choi, D., Lemmon, J.P., and Liu, J. (2011). Electrochemical energy storage for green grid. Chem. Rev. *111*, 3577–3613.
3. Leung, P., Shah, A.A., Sanz, L., Flox, C., Morante, J.R., Xu, Q., Mohamed, M.R., Ponce de León, C., and Walsh, F.C. (2017). Recent developments in organic redox flow batteries: A critical review. J. Power Sources *360*, 243–283.
4. Janoschka, T., Martin, N., Martin, U., Friebe, C., Morgenstern, S., Hiller, H., Hager, M.D., and Schubert, U.S. (2015). An aqueous, polymer-based redox-flow battery using non-corrosive, safe, and low-cost materials. Nature *527*, 78–81.
5. Winsberg, J., Hagemann, T., Janoschka, T., Hager, M.D., and Schubert, U.S. (2017). Redox-flow batteries: from metals to organic redox-active materials. Angew. Chem. Int. Ed. *56*, 686–711.
6. Dinesh, A., Olivera, S., Venkatesh, K., Santosh, M.S., Priya, M.G., Muralidhara, H.B., Inamuddin, and Asiri, A.M. (2018). Iron-based flow batteries to store renewable energies. Environ. Chem. Lett. *29*, 325.
7. Huggins, R.A. (2017). Review—a new class of high rate, long cycle life, aqueous electrolyte battery electrodes. J. Electrochem. Soc. *164*, A5031–A5036.
8. Lin, K., Chen, Q., Gerhardt, M.R., Tong, L., Kim, S.B., Eisenach, L., Valle, A.W., Hardee, D., Gordon, R.G., Aziz, M.J., and Marshak, M.P. (2015). Alkaline quinone flow battery. Science *349*, 1529–1532.
9. Adams, G.B. (1979). Electrically rechargeable battery. US patent US4180623, granted December 19, 1979.
10. Luo, J., Hu, B., Debruler, C., Bi, Y., Zhao, Y., Yuan, B., Hu, M., Wu, W., and Liu, T.L. (2019). Unprecedented capacity and stability of ammonium ferrocyanide catholyte in pH neutral aqueous redox flow batteries. Joule *3*, this issue, 149–163.
11. DeBruler, C., Hu, B., Moss, J., Luo, J., and Liu, T.L. (2018). A sulfonate-functionalized viologen enabling neutral cation exchange, aqueous organic redox flow batteries toward renewable energy storage. ACS Energy Lett. *3*, 663–668.

Preview

Boosting the Single-Pass Conversion for Renewable Chemical Electrosynthesis

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Efficient engineering design of CO_2 and CO electrolysis systems is key to achieving practical renewable energy conversion and storage via the upgrading of CO_2. High selectivity, current density, and energy efficiency have been the focus of many research efforts. The single-pass conversion of the reactants is another crucial system parameter that has—until now—received too little attention. Recently in *Joule*, Ripatti et al. showcase an electrolyzer that achieves high single-pass conversion combined with high current density.

The electrochemical reduction of carbon dioxide (CO_2) to multi-carbon-based products provides a route to accelerate the deployment of renewable electricity and to realize low-carbon-footprint fuels and chemicals.[1] The process can be performed in a single electrochemical reaction; or, alternatively, in a two-step process, such as CO_2 electroreduction to carbon monoxide (CO) followed by CO reduction to multi-carbon chemicals. CO electroreduction offers a route to generate multi-carbon chemicals with high selectivity because it avoids the formation of CO and formic acid, which are common single-carbon products in CO_2 reduction. In addition, CO has the benefit that it does not react with hydroxide ions presented in the electrolytes widely used in CO_2 and CO electrolysis.

Recently in *Joule*, Ripatti et al. demonstrate an electrolysis system that produces concentrated multi-carbon products with high single-pass conversion efficiency at high reaction rate and selectivity. They do so by carefully controlling the reactants and ion transport in a membrane electrode assembly system.[2]

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