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## REDOX FLOW BATTERIES BASED ON SUPPORTING SOLUTIONS CONTAINING CHLORIDE

### CROSS REFERENCE TO RELATED APPLICATIONS

This is a Continuation of U.S. patent application Ser. No. 12/892,693, filed Sep. 28, 2010, which is incorporated by reference.

### STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with Government support under Contract DE-AC0576RL01830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

### BACKGROUND

A redox flow battery (RFB) stores electrical energy in reduced and oxidized species dissolved in two separate electrolyte solutions. The anolyte and the catholyte circulate through a cell electrode separated by a porous membrane. Redox flow batteries are advantageous for energy storage because they are capable of tolerating fluctuating power supplies, repetitive charge/discharge cycles at maximum rates, overcharging, overdischarging, and because cycling can be initiated at any state of charge.

However, among the many redox couples upon which redox flow batteries are based, a number of disadvantages exist. For example, many systems utilize redox species that are unstable, are highly oxidative, are difficult to reduce or oxidize, precipitate out of solution, and/or generate volatile gases. In many ways, the existing approaches to addressing these disadvantages have been ad hoc and can include the imposition of restrictive operating conditions, the use of expensive membranes, the inclusion of catalysts on the electrodes, and/or the addition of external heat management devices. These approaches can significantly increase the complexity and the cost of the total system. Therefore, a need for improved redox flow battery systems exists.

### SUMMARY

The present invention includes redox flow battery systems having a supporting solution that comprises  $\text{Cl}^-$  anions. In one embodiment, a vanadium-based redox flow battery system is characterized by an anolyte comprising  $\text{V}^{2+}$  and  $\text{V}^{3+}$  in a supporting solution and a catholyte comprising  $\text{V}^{4+}$  and  $\text{V}^{5+}$  in a supporting solution. The supporting solution can comprise  $\text{Cl}^-$  ions or a mixture of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  ions. The use of  $\text{Cl}^-$  ions can improve the energy density and the stability of an all-vanadium battery compared to the traditional use of  $\text{SO}_4^{2-}$  ions.

Supporting solutions comprising both  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  ions can further improve the performance and characteristics by all-vanadium batteries by increasing the solubility of the vanadium cations as described in greater detail below. In particular embodiments, the concentration ratio of  $\text{Cl}^-$  to  $\text{SO}_4^{2-}$  can be between 1:100 and 100:1. In other embodiments, the ratio can be between 1:10 and 10:1. In still other embodiments, the ratio can be between 1:3 and 3:1.

For all-vanadium batteries, the  $\text{Cl}^-$  in the supporting solution can improve stability of the vanadium cations. For example, in traditional flow redox batteries,  $\text{V}^{5+}$  can tend to

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form  $\text{V}_2\text{O}_5$  at temperatures above  $40^\circ\text{C}$ . However, the presence of  $\text{Cl}^-$  ions in the supporting solution can result in the formation of  $\text{VO}_2\text{Cl}(\text{H}_2\text{O})_2$ , a stable, neutral species. Accordingly, embodiments of the present invention can operate at cell temperatures greater than  $40^\circ\text{C}$ . Preferably, the cell temperature during operation is between  $-35^\circ\text{C}$  and  $60^\circ\text{C}$ . Furthermore, the embodiments of the present invention can operate without thermal management devices actively regulating the cell temperature. In conventional all-vanadium flow redox batteries, thermal management devices are required to maintain the battery below the cell temperature at which the V cations come out of solution.

Further still, vanadium cation concentrations in batteries of the present invention can exceed those of traditional  $\text{SO}_4^{2-}$ -based batteries. In some embodiments, the vanadium cation concentration is greater than 0.5M. In others, the vanadium cation concentration is greater than 1.7M. In still others, the vanadium cation concentration is greater than 2.5M.

In a preferred embodiment, the state of charge condition is greater than 0% and less than 100% during operation. In other words, the batteries are preferably not operated to full charge or discharge states.

In another embodiment of the present invention, a redox flow battery having a supporting solution comprising  $\text{Cl}^-$  ions comprises an anolyte comprising  $\text{V}^{2+}$  and  $\text{V}^{3+}$  in the supporting solution, a catholyte comprising  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the supporting solution, and a membrane separating the anolyte and the catholyte. The anolyte and catholyte can comprise V cations and Fe cations, respectively, or the anolyte and catholyte can each contain both V and Fe cations in a mixture. In some instances, the concentrations of the Fe cations and/or the V cations can be greater than 0.5M.

Relative to some highly oxidative redox couples, the Fe and V couple is less aggressive. Accordingly, expensive oxidation-resistant membranes such as sulfonated tetrafluoroethylene based fluoropolymer-copolymers are not necessary. On a cost basis, other less expensive options can be preferable. Accordingly, some embodiments of the Fe/V battery system comprise hydrocarbon-based membranes or microporous separators. One example of a hydrocarbon membrane includes, but is not limited to a sulfonated poly(phenylsulfone) membrane. Other ion exchange membranes can be suitable.

In another embodiment, the Fe/V battery system comprises electrodes, which do not contain a redox catalyst, in contact with the anolyte and the catholyte. Redox catalysts are sometimes necessary for species that are difficult to reduce and/or oxidize and can include metals or metal oxides. Redox catalysts are preferably absent from the electrodes used in embodiments of the present invention.

Some embodiments of the Fe/V battery system operate at cell temperatures below  $60^\circ\text{C}$ . In other embodiments, the system operates at cell temperatures between  $-20^\circ\text{C}$  and  $50^\circ\text{C}$ . In preferred embodiments, the system does not include a heat management device actively regulating the cell temperature. In particular, no heat management device is utilized to heat the Fe/V battery system.

In the Fe/V battery systems, supporting solutions comprising both  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  ions can further improve the performance and characteristics by increasing the solubility of the cations as described in greater detail below. In particular embodiments, the concentration ratio of  $\text{Cl}^-$  to  $\text{SO}_4^{2-}$  can be between 1:100 and 100:1. In other embodiments, the ratio can be between 1:10 and 10:1. In still other embodiments, the ratio can be between 1:3 and 3:1. Instances in which the supporting solution comprises both  $\text{Cl}^-$  to  $\text{SO}_4^{2-}$  and the anolyte and catholyte both comprise V and Fe cations, the