

1

HYBRID ANODES FOR REDOX FLOW BATTERIES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation in part of currently pending U.S. patent application Ser. No. 13/532,206 filed on Jun. 25, 2012 and of currently pending U.S. patent application Ser. No. 13/912,516 filed on Jun. 7, 2013, which is a continuation in part of U.S. patent application Ser. No. 13/439,083 filed on Apr. 4, 2012, now U.S. Pat. No. 9,130,218B2. The disclosures of the related applications are incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with Government support under Contract DE-AC0576RLO1830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

BACKGROUND

Practical implementation of a number of important technologies has been slowed by limitations in state-of-the-art energy storage devices. For instance, energy storage devices having electrodes comprising metals, such as Li, Na, Zn, Si, Mg, Al, Sn, and Fe, often face the challenges of dendrite growth and unstable solid electrolyte interface (SEI) layers, which can lead to cell shorting and combustion—thus presenting a major safety concern, especially at high charge rates (current density). In one example, lithium sulfur based redox flow batteries (RFB) using lithium metal as an anode and a LixSy solvent or suspension electrolyte as a catholyte are attractive because of the large specific capacity and energy density. However the formation of soluble long chain polysulfides during charge/discharge can lead to the gradual loss of active mass from the cathode into the electrolyte and onto the lithium anode, continuously forming a passivation film. As a result, severe self-discharge and capacity decay upon cycling are usually observed, hindering the practical application of lithium sulfur batteries. In another example, Li-based non-aqueous RFBs, which can exhibit high energy density and high energy efficiency, can suffer from relatively unstable anodes that limit the cycle life of the RFB. The anode instability can be caused by dendrite growth and/or failure of the solid electrolyte interface (SEI) layer. Traditional approaches of using electrolyte additives or physical barriers to protect the metal anode are often inadequate for the operating conditions possible in certain RFBs. For example, some Li-based nonaqueous RFBs can operate at current densities that are at least ten times higher than conventional, non-flowing lithium-ion batteries. Therefore, improved energy storage devices with stable electrochemical performance and improved safety are needed to enable devices requiring electrical power as well as those benefiting from efficient energy storage.

SUMMARY

This document describes methods of operating RFBs, as well as RFB devices having solid hybrid electrodes that address, at least in part, the problem of electrode instability associated with dendrite growth and/or SEI layer failure. The solid hybrid electrode can result in the shifting of the interfacial redox reaction away from the surface of the electroactive

2

electrode. Accordingly, embodiments described herein can exhibit long and stable cycling at high current densities. RFB, as used herein, can refer to a single cell or a stack of cells, wherein each cell comprises a first half cell, a second half cell, and terminals allowing current to flow into and out of the cell. Each half cell can comprise an electrode and/or an electrolyte. A half-cell can further comprise a current collector.

The embodiments described herein comprise a first half cell separated by a separator or membrane from a second half cell containing the solid hybrid electrode. The first half cell comprises a first redox couple dissolved in a solution or contained in a suspension. The solid hybrid electrode comprises a first electrode electrically connected to a second electrode, thereby resulting in an equipotential between the first and second electrodes. The electrical connection can be a physical connection by contact and/or through a wire or connector. Some embodiments can further comprise a reservoir containing a supply of the first redox couple dissolved in the solution or contained in the suspension, the reservoir connected to the first half cell via a conduit and a flow regulator. Other embodiments, alternatively or in addition, can further comprise a fluid circulator to induce flow in an electrolyte in the second half cell.

As used herein, equipotential can encompass minor deviations from a theoretical equipotential (i.e., a pseudo-equipotential). For example, the first electrode and second electrode should, in principle, have the same potential. However, in some instances, it can take significant time to reach equilibrium and equal potential. Thus, the potentials of the first and second electrodes may be very close, but may not be quite equal. In preferred embodiments, the potential differences between the first and second electrode is negligible.

In one sense, the first and second electrodes are connected in parallel to function as an electrode. The first and second electrodes can be separated by a separator or membrane or can be exposed directly one to another. Furthermore, the first and second electrodes can be in direct contact or can be separated by some volume. In particular embodiments, the first and second electrodes remain in contact during operation and not merely prior to initial cycling. For example, the second electrode is not merely an initial source of electroactive metal to be incorporated into the first electrode (i.e., intercalated, deposited, etc.). According to one embodiment, the first electrode functions as a drain for metal ions and helps to decouple the contamination problem, or undesired reactions, on the second electrode throughout operation of the device.

The first electrode comprises a conductive solid material and the second electrode comprises a solid electroactive metal. In one embodiment, the first electrode comprises a carbon electrode. Examples of carbon electrodes include, but are not limited to, conductive carbon materials such as graphite, hard carbon, carbon black, carbon fibers, graphene, graphite felt, carbon nanotubes, and combinations thereof. The second electrode comprises a solid electroactive metal. Examples of solid electroactive metals can include, but are not limited to, Li, Na, K, Zn, Si, Mg, Ca, Al, Sn, Fe, and combinations thereof.

According to various embodiments, the redox couple can comprise a redox active organic, inorganic, or organometallic compound. Examples of redox active organic compounds can include, but are not limited to, TEMPO, anthroquinones, DBBB, sulfides, disulfides, polysulfides, nitroxyl radicals, galvinoxyl radicals, carbonyl compounds, quinones and quinone derivatives, TEMPO, metallocenes ferrocenes, carbazoles, tertiary amines, 2,5-di-tert-butyl-1,4-dialkoxybenzenes, quinoxalines, phthalocyanines, porphyrins, pyrazines, and combinations thereof. Examples of redox active inor-