



Improvement and analysis of the hydrogen-cerium redox flow cell



Michael C. Tucker*, Alexandra Weiss, Adam Z. Weber

Energy Conversion Group, Energy Technologies Area, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd, Berkeley, CA 94720, USA

HIGHLIGHTS

- The H₂-Ce RFB performance is improved using commercially-available materials.
- Maximum discharge power of 0.9 W cm⁻² was observed at 60 °C.
- Energy efficiency of 90% was achieved at 50 °C.

ARTICLE INFO

Article history:

Received 29 April 2016

Received in revised form

25 July 2016

Accepted 26 July 2016

Available online 3 August 2016

Keywords:

Redox flow battery

Cerium

Hydrogen

Methanesulfonic acid

ABSTRACT

The H₂-Ce redox flow cell is optimized using commercially-available cell materials. Cell performance is found to be sensitive to the upper charge cutoff voltage, membrane boiling pretreatment, methanesulfonic-acid concentration, (+) electrode surface area and flow pattern, and operating temperature. Performance is relatively insensitive to membrane thickness, Cerium concentration, and all features of the (-) electrode including hydrogen flow. Cell performance appears to be limited by mass transport and kinetics in the cerium (+) electrode. Maximum discharge power of 895 mW cm⁻² was observed at 60 °C; an energy efficiency of 90% was achieved at 50 °C. The H₂-Ce cell is promising for energy storage assuming one can optimize Ce reaction kinetics and electrolyte.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Redox flow batteries (RFB) with various solution chemistries are being developed for large-scale energy storage [1–5]. Advances in redox-active species, electrocatalysts, and separators are required to meet the stringent cost and durability requirements for affordable storage, and recent years have seen many new contributions to the field, which also highlight the necessary areas for improvement [2]. One promising class of RFB utilizes hydrogen gas as the negative working fluid, and an aqueous solution of redox-active species as the positive working fluid. Hydrogen is inexpensive, can be electrochemically compressed to minimize storage volume, and has excellent reaction kinetics. Liquid that crosses through the membrane from the (+) to (-) side is easily separated from the hydrogen gas for return to the positive-electrode tank, simplifying electrolyte balancing. With only one side of the cell containing liquid, pumping and shunt-current losses are expected to be minimized.

Furthermore, the adoption of cell architecture derived from mature high-power proton-exchange-membrane (PEM) fuel cells provides excellent cell performance metrics.

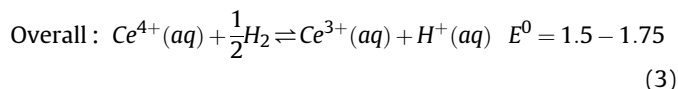
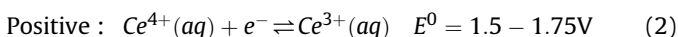
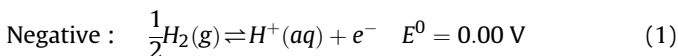
Various RFBs with hydrogen (-) electrode have been reported. Hydrogen-halogen cells using primarily Cl₂ and Br₂ have been reviewed recently, and provide among the highest reported power and efficiency metrics for RFBs due to fast, reversible kinetics and moderate self-discharge [6,7]. For example, 1.4 W cm⁻² discharge power density, 90% peak energy efficiency, and 80% energy efficiency at 0.4 A cm⁻² were achieved at room temperature for the H₂-Br₂ system, which has an open circuit voltage (OCV) of 1.09 V [8,9]. The H₂-Fe cell provides the potential for extremely inexpensive and benign iron-based electrolyte, however at a rather low cell potential (0.77 V) [10–12]. Optimization of this cell, including addition of supporting electrolyte, achieved peak power density of 250 mW cm⁻² and energy storage efficiency of 78% [10]. Cost analysis suggested that although the active materials are very inexpensive, cell performance was too low to be economically attractive given the cost of cell/stack materials. The H₂-V system offers open-circuit potential of 1–1.2 V, depending on vanadium concentration. Proof-of-concept work demonstrated moderate performance (114 mW cm⁻²) and 60% energy efficiency [13]. The

* Corresponding author. LBNL, 1 Cyclotron Rd, MS 70-108B, Berkeley, CA 94720, USA.

E-mail address: mctucker@lbl.gov (M.C. Tucker).

main limitations for this cell are thought to be vanadium diffusion in the (+) electrode and interaction of crossover vanadium with the Pt (–) catalyst [14]. The H₂–Ce system provides unusually high open circuit voltage (1.5–1.7 V), which could enable high power and energy densities. A proof-of-concept for this system demonstrated 148 mW cm^{–2} peak discharge power and 88% energy efficiency, and suggested that cerium kinetics limits cell performance [15]. The Ce (+) electrode operates at potentials outside the stability window of water; however, extensive work on the aqueous Zn–Ce RFB indicates that appropriate solution chemistry and operating protocols can mitigate deleterious oxygen evolution [16]. Due to its potential for high energy and high power densities, this cell is explored in this paper to see if a more optimized system is promising.

The H₂–Ce redox-flow system consists of an electrochemical cell that is fed reactants from storage tanks containing gaseous hydrogen (negative side) and an aqueous solution of Ce⁴⁺ (positive side), as shown in Fig. 1. During discharge, hydrogen is oxidized to protons at the negative electrode. The protons pass through an ion-conducting membrane and balance the reduction of Cerium(IV) methanesulfonate to Cerium(III) methanesulfonate at the positive electrode, and methanesulfonic acid (MSA) is released into solution from the Cerium(IV) methanesulfonate complex. The electrochemical reactions are shown below with the forward direction corresponding to discharge and the reverse to charge. Note that the potential for Reaction 2 depends on solvent type and concentration [16,17].



The promise of the high OCV offered by the H₂–Ce couple is tempered by the relatively low current density reported for aqueous cerium electrochemistry on Pt catalyst in general [16–20], and moderate power density demonstrated for the H₂–Ce cell specifically [15]. In this work, we optimize the cell architecture and materials to achieve significantly improved power density and efficiency with commercially-available materials, and find that future improvements may require development of new cerium electro-

catalysts and electrode architectures.

2. Experimental methods

Cells were assembled and tested using 10 cm² Fuel Cell Technologies hardware and equipment discussed in detail elsewhere [8,9,21,22]. A graphite serpentine flow field was used on the negative side (Fuel Cell Technologies). Serpentine or flow-through Niobium flowfields were used on the positive side to avoid carbon oxidation or metal corrosion (Treadstone Technologies, Inc.). The (+) electrode material was Pt woven mesh (Alfa Aesar, 0.17 mm thick, 52 mesh, 0.1 mm diameter wire), Ti woven mesh (Alfa Aesar, 0.22 mm thick, 50 mesh, 0.102 mm diameter wire), platinumized titanium expanded mesh (Metakem type G, 4 × 2 mm diamond holes between 0.5 × 0.5 mm strands), platinumized niobium expanded mesh (Gold Plating Services, 3 × 1.5 mm diamond holes between 0.3 × 0.15 mm strands), or nanostructured thin-film (NSTF) platinum catalyst layer (3M Company). The (–) electrode was 0.4 mg/cm² Pt/C printed on Sigracet GDL 24BC gas-diffusion layer (GDL), provided by Ion Power. Nafion 212 membranes were used, except where noted. Membranes were pretreated by boiling successively in 3% H₂O₂, DI water, 0.5 M sulfuric acid, and DI water for 1 h each, except where noted. The peroxide boiling step was skipped for NSTF-coated samples. Boiled membranes were assembled into the cell in the hydrated state to maximize conductivity [22], as crossover was found not to be a dominant concern for this system, as discussed in Section 3.2.3. Thickness of the incompressible gaskets around the active cell materials was chosen to achieve 20–25% compression of the (–) electrode upon assembly.

Cells were operated with hydrogen bubbled through water (200 mL min^{–1}) and 0.6 M cerium methanesulfonate with 3–6 M MSA solution (150 mL min^{–1}), except where noted. Solution volume for polarization curves was 300 mL, and for efficiency mapping was 20 mL. Hydrogen pressure was controlled with a backpressure regulator on the cell exhaust line. The (–) hydrogen exhaust was passed through a closed-bottom tube to collect any crossover liquid coming through the membrane from the (+) side; however, typically no liquid was observed, and the (–) electrode was found dry upon cell disassembly. Polarization curves (5–30 mA/cm² steps of 10 s each), AC impedance (at OCV), and cycling efficiency curves according to a protocol discussed elsewhere [11,21] (typically with voltage limits of 0.2–1.9 V), were obtained with a Bio-Logic VMP3 potentiostat. AC impedance was taken by discharging at 120 mA cm^{–2} while scanning from 200 kHz to 10 Hz with 1 mA cm^{–2} perturbation. Before testing, solutions were charged by holding the cell at 2 V until the theoretical charge required for 100% state of charge was achieved (the charging current also dropped significantly at the end of charge). Cerium utilization was determined from coulometry during cell operation. For each current density of interest, the cell was charged and then discharged, and the discharge capacity was used to determine the amount of cerium utilized, which was then compared to the total amount available (calculated from solution volume and concentration). Elevated-temperature experiments were conducted with cartridge heaters and a thermocouple in the cell hardware, and the solution tank submerged in a heated water bath.

Various cerium salts were screened for use in solution preparation. Solutions were prepared by adding the salt to water, and then slowly adding MSA. Cerium nitrate and cerium sulfate were ruled out based on observation of low solubility. Cerium carbonate was the most favorable, as it dissolved completely and produced a clear solution after off-gassing CO₂ via the conversion to cerium methanesulfonate. For 0.6 M Ce solutions, greater than 1 M MSA was required to achieve complete dissolution, and MSA concentrations in the range of 2–6 M were tested. For 4 M MSA, a range of

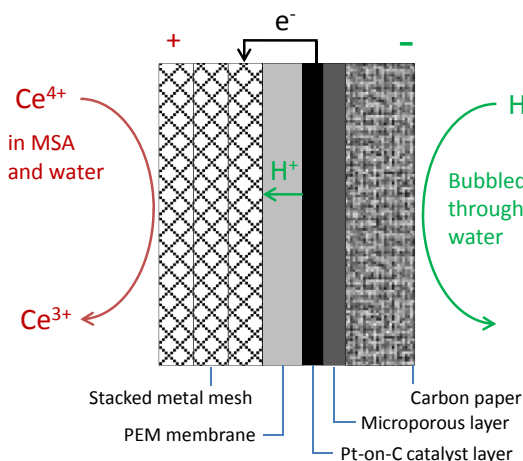


Fig. 1. Schematic of H₂–Ce redox flow cell.

Download English Version:

<https://daneshyari.com/en/article/7727140>

Download Persian Version:

<https://daneshyari.com/article/7727140>

[Daneshyari.com](https://daneshyari.com)