Electrochimica Acta 56 (2011) 6536–6546

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Zinc deposition and dissolution in methanesulfonic acid onto a carbon composite electrode as the negative electrode reactions in a hybrid redox flow battery

P.K. Leung, C. Ponce-de-León*, C.T.J. Low, F.C. Walsh

Electrochemical Engineering Laboratory, Energy Technology Research Group, University of Southampton, Highfield, Southampton, SO17 1BJ, United Kingdom

ARTICLE INFO

Article history:
Received 24 January 2011
Received in revised form 26 April 2011
Accepted 27 April 2011
Available online 6 May 2011

Keywords:
Dendrite
Electrodeposition
Flow battery
Methanesulfonic acid
Zinc

ABSTRACT

Electrodeposition and dissolution of zinc in methanesulfonic acid were studied as the negative electrode reactions in a hybrid redox flow battery. Cyclic voltammetry at a rotating disk electrode was used to characterize the electrochemistry and the effect of process conditions on the deposition and dissolution rate of zinc in aqueous methanesulfonic acid. At a sufficiently high current density, the deposition process became a mass transport controlled reaction. The diffusion coefficient of Zn^{2+} ions was 7.5×10^{-6} cm^2 s^{-1}. The performance of the zinc negative electrode in a parallel plate flow cell was also studied as a function of Zn^{2+} ion concentration, methanesulfonic acid concentration, current density, electrolyte flow rate, operating temperature and the addition of electrolytic additives, including potassium sodium tartarate, tetrabutylammonium hydroxide, and indium oxide. The current-, voltage- and energy efficiencies of the zinc-half cell reaction and the morphologies of the zinc deposits are also discussed. The energy efficiency improved from 62% in the absence of additives to 73% upon the addition of 2×10^{-3} mol dm^{-3} of indium oxide as a hydrogen suppressant. In aqueous methanesulfonic acid with or without additives, there was no significant dendrite formation after zinc electrodeposition for 4 h at 50 mA cm^{-2}.

1. Introduction

Power generation sources need to develop energy storage capabilities to be more efficient during off-peak hours [1]. Excess power generation and transmission are underused every year due to insufficient energy storage leading to problems, such as raised volatility, reduced reliability and energy wastage [1,2]. The increasing interest in renewables has drawn attention to the fact more reliable, affordable, flexible and safer energy storage systems are required.

Recently, redox flow batteries have emerged as possible systems for energy storage. Some advantages over conventional energy storage systems are that they can be installed anywhere, as standalone systems and no special terrain or climate is necessary. Compared to the conventional lead acid battery, redox flow batteries are less costly to maintain. The modular nature of the redox flow battery enhances its transportability and makes its construction and maintenance costs, lowest among other energy storage systems [3]. Since 1970, a number of redox flow batteries have been developed for applications in bulk energy storage, load-levelling, strategic power supplies and electric vehicles. Due to the electronegativity of zinc, its large negative potential in aqueous medium and its widespread availability, the zinc redox couple has been considered as the negative electroactive species in redox flow batteries.

The large negative potential of the zinc redox couple allows a high energy density when coupled with other electropositive redox couples, such as chlorine/chloride [4,5], bromine/bromide [6,7], ferrocyanide/ferricyanide (hexacyanoferrate II/III) [8], ceric/cerous [9] and oxygen/water [10]. The combination of zinc with these couples facilitates a high energy density. During the charge–discharge cycle of a redox flow battery, the electrodeposition of zinc:

$$\mathrm{Zn(II)} + 2\mathrm{e}^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} \mathrm{Zn} \quad E^\circ = -0.76\,\mathrm{V}\ vs.\ \mathrm{SHE} \tag{1}$$

is the reaction at the negative electrode.

In the case of a zinc–cerium hybrid redox flow battery, the positive electrode reaction is [11]:

$$\mathrm{Ce(III)} - \mathrm{e}^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} \mathrm{Ce(IV)} \quad E^\circ \approx +1.28 - 1.72\,\mathrm{V}\ vs.\ \mathrm{SHE} \tag{2}$$

The range of the cell potential difference for this pair of redox couples depends on the type of electrolyte used. According to Plurion Inc. (UK), the open-circuit cell voltage of a zinc–cerium flow battery can be up to 2.4 V [12]. Recent attention has focused on the application of aqueous methanesulfonic acid as an electrolyte

* Corresponding author. Tel.: +44 23 80598931; fax: +44 23 80597051.
E-mail address: capla@soton.ac.uk (C. Ponce-de-León).

0013-4686/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2011.04.111

for redox flow batteries, as this electrolyte allows a high solubility for a wide range of metal ions, including the highly electropositive lead [13] and cerium ions [14]. Methanesulfonic acid has comparable conductivity and is generally less corrosive than other common electrolytes, such as sulfuric and hydrochloric acids [13].

Although zinc electrodeposition has been practised for a long time using acidic chloride [15–21] and sulfate [22–25] baths, there have been few studies of zinc electrodeposition from methanesulfonic acid electrolytes [26]. Recent patents have suggested that methanesulfonic acid can significantly decrease the dendritic growth [10,27], thus increasing the life cycle in a zinc-based flow battery. In contrast to the electroplating industry, where the majority of the substrates are metals, carbon-based materials are the commonest electrode materials used in redox flow batteries [28–30], as in many cases they are chemically inert and do not undergo dissolution and formation of oxides. In this work, the electrochemistry of zinc in methanesulfonic acid was studied via cyclic voltammetry at a glassy carbon rotating disk electrode. In order to optimize the conditions for a zinc-based redox flow battery, a range of electrodeposition and dissolution experiments have been carried out in a parallel plate flow-cell using different electrolyte compositions and operating parameters. A detailed discussion of zinc morphology and system efficiency is included in this study.

2. Experimental details

2.1. Chemicals

All chemicals used were analytical reagent grade from Alfa Aesar (UK) and Sigma Aldrich (Germany); the solutions were prepared with ultra-pure water (18 MΩ cm resistivity) from an Elga water purification system. The solutions were purged with a fast stream of dispersed nitrogen gas (The BOC Group, UK) for 10 min to avoid interference from the oxygen reduction reaction. Zinc(II) methanesulfonate solutions were produced by stirring zinc carbonate basic (Alfa Aesar, UK, 99 wt.%) using a PTFE-coated steel magnetic stirred bar (Fisherband, UK, 1 cm diameter, 4 cm length) in 70% methanesulfonic acid (Sigma Aldrich, Germany). The resulting zinc methanesulfonate solutions were colourless, clean solutions with no precipitate. All electrolytic additives were laboratory grade, supplied by Fluka (Austria) or Sigma Aldrich (Germany).

2.2. Cyclic voltammetry

Cyclic voltammetry was carried out in a divided, three-electrode glass cell. The electrolyte volume contained in the working electrode compartment was approximately 100 cm^3. The glass cell was equipped with a water jacket connected to a Grant LV FG water thermostat to control the electrolyte temperature in the range of 20–60 °C. The working electrode was a static glassy carbon disk electrode (area: 0.13 cm^2) while the counter electrode was a large area platinum mesh (projected area: 1 cm^2). The working and counter electrode compartments were separated by a Nafion® membrane (Dupont, NF115/H^+). The electrode potential was measured against a saturated silver/silver chloride electrode (ABB, Series 1400, 1.0 mol dm^{-3} KNO_3). For the cyclic voltammetry, the potential was linearly swept from −0.8 to −1.4 V *vs.* Ag|AgCl at a potential sweep rate in the range from 8 to 128 mV s^{-1}. Cyclic voltammograms were recorded over a wide range of electrolyte composition including 10–80 mmol dm^{-3} zinc methanesulfonate in 0.5 mol dm^{-3} sodium methanesulfonate solution adjusted to pH 0–4 with methanesulfonic acid. All electrochemical measurements were made with an EcoChemie Autolab (PGSTAT20) computer controlled potentiostat using the General Purpose, Electrochemical Software (GPES) Version 4.5.

2.3. Electrolysis in a flow cell

Electrodeposition and dissolution of Zn in methanesulfonic acid were carried out in a divided, parallel plate flow cell. A cation-conducting Nafion® membrane (DuPont, NF117/H^+) separated the two compartments. Carbon polyvinyl-ester composite (BMC 18649, Engtegris GmbH, Germany) was used for both the negative and the positive electrodes. Each electrode had an area of 4.5 cm × 2 cm (9 cm^2) with a gap of 2.0 cm between the electrode surface and the membrane. The volume of each electrolyte contained in separated tanks was 100 cm^3. Both positive and negative electrolytes were circulated at a mean linear flow velocity between 1.8 and 7.8 cm s^{-1} through the cell using a peristaltic pump (Masterflex® Model 7553079, Cole-Parmer) with high-pressure tubing (Masterflex® Norprene®, Cole-Parmer). The negative electrode compartment contained 0.5–2 mol dm^{-3} zinc methanesulfonate in 0.5–3 mol dm^{-3} methanesulfonic acid while the positive electrode compartment contained 1.0 mol dm^{-3} methanesulfonic acid. The temperature of both electrolytes was controlled at (293–343) ± 2 K by thermostat (Grant Model LV FG) and circulated water through jackets fitted to each electrolyte reservoir.

At the negative electrode, zinc was electrodeposited at current density in the range of 20–80 mA cm^{-2} for 4 h. The electrode was then left at open-circuit for 1 min followed by zinc dissolution using the same current density. The electrolysis during the oxidation stopped when the zinc half-cell voltage shifted towards more positive values than 0 V *vs.* Ag|AgCl to avoid the oxidation of the substrate material. The reference electrodes were saturated silver–silver chloride electrode, Ag|AgCl (ABB, Series 1400, 0.1 mol dm^{-3} KNO_3) placed at the entrance of the flow cell in each channel. The electrochemical measurements were made by BaSyTec (5 A/12 V, Germany) battery test system. The anode- and cathode-potentials together with the cell potential difference were continuously monitored throughout the experiment.

2.4. Electrodeposition and microscopy

Zinc electrodeposition in the presence and absence of additives was carried out in an electrolyte containing 1.5 mol dm^{-3} zinc methanesulfonate and 1 mol dm^{-3} methanesulfonic acid electrolyte (60 cm^3) in a 100 cm^3 glass beaker. The applied current density was 50 mA cm^{-2} for 4 h. Carbon polyvinyl-ester composite (Engtegris Inc., BMC 18649, Germany) electrodes of 8 cm × 1 cm dimensions and with an exposed electrode area of 4 cm × 1 cm were used as both cathode and anode. The electrodes faced each other when fitted into a nylon holder with an interelectrode gap of 1 cm. Before each experiment, the electrodes were polished using silicon carbide paper (grade P120), degreased with detergent then left in an ultrasonic bath for 10 min in deionized water. The electrode holder was immersed in a double walled water jacket container that allows water circulation from the bath thermostat to maintain the temperature of the solution constant, typically at 50 °C.

Throughout the experiment, the solution was stirred at 400 rpm using an IKa yellowline® magnetic stirrer. After the electrodeposition and before taking the microscopic images, the samples were rinsed with ultrapure water (Elga water purification system) for 10 s, air-dried and stored in a sample bag placed in a container with silica gel granules. The images of the zinc electrodeposits were taken with a JEOL scanning electron microscope (model JSM 6500 F) equipped with an energy-dispersive X-ray spectroscopic analyzer, which was used to estimate the elemental composition.