



Electrodeposition and electrodisolution of zinc in mixed methanesulfonate-based electrolytes

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ABSTRACT

Zinc electrodeposition and electrodisolution in methanesulfonic acid (MSA) electrolytes mixed with chloride or sulfate are investigated in a 3-electrode cell for eventual use in divided and undivided zinc-cerium redox flow batteries (RFB). Cyclic voltammetry and polarization experiments show that the addition of chloride to methanesulfonate-based electrolytes shifts the nucleation potential in the positive direction, lowers the nucleation overpotential and enhances the kinetics of Zn deposition and subsequent dissolution relative to that achieved when sulfate is added or MSA is the only anion present. In addition, the diffusion coefficient of Zn(II) and the resulting limiting current density for Zn deposition have been found to be moderately higher in mixed methanesulfonate/chloride media than when chloride is absent. The effects of temperature, MSA concentration, Zn(II) concentration and current density on the Zn/Zn(II) system have also been investigated under potentiostatic and galvanostatic conditions. Although an increase in temperature and/or MSA concentration tends to lower the charge efficiency for Zn deposition in both mixed and MSA-only electrolytes due to the higher rate of hydrogen evolution, the amount of zinc deposited, charge and voltage efficiency always remain significantly higher in the mixed methanesulfonate/chloride media than the pure MSA media. Thus, the use of a mixed methanesulfonate/chloride media should enable both divided and undivided zinc-cerium RFBs to operate over a wider range of temperatures and MSA concentrations compared to the case with pure MSA electrolyte. The addition of sulfate to MSA-based electrolytes, however, does not improve the performance of the Zn/Zn(II) system relative to that possible in the MSA-only electrolytes.

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1. Introduction

In the last few years, the interest in energy storage devices has intensified [1,2]. A reliable and cost-effective energy storage unit can dramatically enhance the integration of renewable energies such as solar and wind into the electrical grid and can smooth out the large inherent fluctuations in the availability of these sources. The energy produced from renewable sources under the proper conditions (time and climate) can be stored in a storage unit and discharged during periods of high demand. If successful, these storage devices will enable the electrical grid to be far less reliant on energy sources such as fossil fuels that are responsible for major environmental problems (climate change, acid rain, air pollution).

One of the most recent and promising technologies for energy storage are redox flow batteries (RFB). Since the active material in

RFBs is stored externally from the cell in storage tanks, the energy and power of such batteries are independent and so they can be scaled up more easily than other types of storage devices [3]. Over the past decades, different RFB systems have been developed. Among these systems, zinc-based RFBs have gained a great deal of attention due to the availability and low price of zinc and the successful use of zinc electrodes in many other battery systems. More importantly, the zinc redox couple provides a large negative potential in aqueous media with a two-electron transfer reaction. Zinc-cerium RFBs are relatively new systems developed by Plurion Inc [4]. This system offers the highest open-circuit voltage (2.4 V) among the other RFBs, which can lead to high energy densities when the electrolyte contains high concentrations of the electroactive species. In this battery, methanesulfonic acid (MSA) has been used as the supporting electrolyte for both the negative Zn/Zn(II) and positive Ce(III)/Ce(IV) half-cells. Divided two-compartment zinc-cerium RFB cells have been operated with 0.8 mol dm⁻³ cerous methanesulfonate dissolved in 4 mol dm⁻³ MSA for the positive half-cell and 1.5 mol dm⁻³ zinc methanesulfonate in

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1 mol dm⁻³ MSA for the negative half-cell [5]. Lower MSA concentrations are used in the negative half-cell since higher concentrations lead to lower zinc deposition/dissolution efficiencies due to competition from the hydrogen evolution reaction [6]. This battery has been operated at 40–60 °C [7] due to the higher reversibility and improved kinetics of the Ce(III)/Ce(IV) redox couple at higher temperatures [7,8].

Despite these advantages, the zinc-cerium system faces a number of obstacles that must be overcome if RFBs based on this chemistry are to become commercially feasible. This has led to considerable research activity on this system in recent years. Despite its favorable thermodynamics, the Ce(III)/Ce(IV) redox reaction has sluggish kinetics [7]. The solubility of Ce(III) rises as the MSA concentration is reduced, whereas the solubility of Ce(IV) is affected in the opposite way [9]. Thus, a compromise must be made to maintain high solubility of both cerium species in the electrolyte. In order to improve the reversibility and kinetics of the Ce(III)/Ce(IV) redox couple and solubility of both cerium species, the use of a mixed-electrolyte media has been investigated as a potential remedy [10,11]. The addition of moderate concentrations (0.5–1 mol dm⁻³) of hydrochloric acid to the base MSA electrolyte has been shown to significantly improve the reversibility and kinetics of the Ce(III)/Ce(IV) redox reaction [11]. Moreover, the diffusion coefficient of Ce(III) was also found to be enhanced in these mixed electrolytes [11]. Although the presence of sulfate rather than chloride in mixed methanesulfonate media also has a positive influence on the Ce(III)/Ce(IV) reaction, its effect does not appear to be as strong [11]. One beneficial effect is an increase in the solubility of Ce(IV) to 1.0 mol dm⁻³ in 2 mol dm⁻³ methanesulfonate/0.5 mol dm⁻³ sulfate solution [10], while it is less than 0.5 mol dm⁻³ in 2.5 mol dm⁻³ pure MSA electrolyte [9]. The introduction of a mixed acid media has also been used in all-vanadium redox flow batteries and also found to have positive effects [12,13]. A mixed chloride/sulfate electrolyte enhanced the operating temperature range and stability of vanadium species which was attributed to the formation of stable and soluble vanadium-chloride intermediate complexes [14].

Leung et al. have investigated the use of a membrane-less single compartment zinc-cerium RFB [15]. Elimination of the expensive ion-exchange membrane from RFBs is a very attractive option since it would significantly reduce the cost of materials, simplify the design of the battery and reduce the ohmic resistance across the cell. Moreover, the proposed undivided zinc/cerium RFB is operated at room temperature [15], which is more desirable than the 50 °C considered for a divided zinc/cerium RFB [5]. As mentioned before, a high MSA concentration is required for a high solubility of Ce(IV) [9], while the efficiency of zinc deposition/dissolution reaction decreases at high MSA concentrations due to excessive hydrogen evolution [6]. Thus, in a membrane-less battery where a single electrolyte is used, a compromise must be made between a high Ce(IV) solubility and high efficiency of the Zn/Zn(II) redox reaction. Consequently, membrane-less zinc-cerium RFBs have been operated at lower acid concentrations (~ 0.2 mol dm⁻³– 0.5 mol dm⁻³) and lower Ce concentrations (0.2 mol dm⁻³– 0.4 mol dm⁻³ Ce(III)) [15,16]. The most successful undivided battery to date has reportedly achieved a current efficiency of 90% and an energy efficiency of 75% at 20 mA cm⁻² [15].

As mentioned previously, mixed-acid media, particularly MSA-chloride electrolyte, have been shown to significantly enhance the reversibility and kinetics of the Ce(III)/Ce(IV) half-cell reaction [11]. Hence, we expect that it would be beneficial to use such mixed-acid media in a membrane-less zinc-cerium RFB as well. Since both electrodes and half-cells are exposed to the same

electrolyte in a membrane-less RFB, it is essential to first investigate the influence of such mixed electrolytes on the zinc deposition and dissolution reactions that occur at the negative electrode during the charge and discharge of a zinc-cerium RFB.

The Zn/Zn(II) half-cell reaction has been studied in methanesulfonic [6,17], sulfuric [18–21] and chloride [21–23] baths. However, to the best of our knowledge, no study on this system in a mixed electrolyte has been reported. The standard rate constant reported in pure chloride solutions is $8.78 \times 10^{-3} \text{ cm s}^{-1}$ [24], which is about an order of magnitude higher than the value of $0.16 \times 10^{-3} \text{ cm s}^{-1}$ obtained in MSA-only electrolytes [25]. This reflects the beneficial role of chlorides in enhancing the kinetics of the zinc redox reaction. Based on the well-known behavior of metal deposition systems in general, we expect that the addition of chloride ions to the base MSA electrolyte will be beneficial to zinc deposition. It has been reported that the presence of chloride in zinc electro-winning baths leads to lower polarization resistance and higher charge efficiency of zinc deposition [26]. Additionally, cyclic voltammetry experiments have shown that the overpotential is reduced and the cathodic peak potential is shifted in the positive direction when zinc deposition is carried out in chloride-only baths rather than sulfate-only electrolytes [21]. Chloride ions have also improved the deposition performance of other metals and alloys such as nickel [27], copper [28], chromium [29], indium [30] and Co-Ni alloys [31]. Thus, it is reasonable to investigate the use of chloride ions to facilitate the zinc deposition process.

In terms of the effect of electrolyte composition on zinc electro-dissolution, a thermometric study has shown that both chloride and sulfate tend to promote the oxidation of zinc in acidic media and should be considered as corrosive anions although it was not possible to easily differentiate between their relative strengths as corrosion promoters [32]. Although the effect of chloride on zinc dissolution in highly acidic methanesulfonate-based electrolytes has not been reported to date, halogens including chloride have been shown to increase the rate of the Zn(II)/Zn(Hg) reduction and oxidation reaction when they are added to a NaClO₄ base electrolyte [33,34].

In this experimental study, we use a 3-electrode system to determine the electrolyte composition and operating conditions that optimize the kinetics of zinc electrodeposition and electro-dissolution in mixed-electrolyte media with particular emphasis on methanesulfonate/chloride solutions. Carbon electrodes have been commonly used in RFB systems due to their chemically inert nature. In some applications, the carbon electrode must be coated to avoid corrosion by corrosive ions (i.e. cerium in the case of an undivided zinc cerium RFB). Moreover, the negative electrode can be modified to inhibit undesired side reactions. For example, indium-modified graphite electrodes can be used on the negative side of the zinc-cerium RFBs to reduce hydrogen evolution [35]. In this work, we use a glassy carbon disk electrode as the working electrode. Since the ultimate aim is to determine the optimum operating conditions for a zinc-cerium RFB, we apply compositions that are typically used for this application. The undivided zinc-cerium RFBs are operated at lower acid concentrations (~ 0.2 mol dm⁻³– 0.5 mol dm⁻³ MSA base electrolyte) [15,16], while the negative half-cell of a divided zinc-cerium RFB typically contains a higher acid concentration of ~ 1 mol dm⁻³ MSA. Thus, in order to address both possible situations, we investigate Zn electrodeposition/electrodissolution in two sets of solutions containing either 0.2 mol dm⁻³ or 1 mol dm⁻³ MSA base electrolyte. In particular, the effects of temperature, acid concentration and Zn(II) concentration on the behavior of the Zn/Zn(II) system in mixed-electrolyte media are determined.

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