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Indium modified graphite electrodes on highly zinc containing methanesulfonate electrolyte for zinc-cerium redox flow battery

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ABSTRACT

The zinc deposition and dissolution reaction in methanesulfonic acid (2.5 mol L^{-1} Zn(II) in 6.5 mol L^{-1} MSA) on indium modified graphite electrodes aiming to suppress the competing hydrogen evolution reaction (HER), was studied on the negative electrode reaction in the zinc-cerium redox flow battery. Cyclic voltammetry, Tafel extrapolation and electrochemical impedance spectroscopy found that elevated temperatures 40 °C improved the kinetics ($j_o = 1 \times 10^{-2}$ A cm^{-2}) of the zinc reaction and shifted the nucleation potential positively by 65 mV. The modified graphite electrodes exhibited higher coulombic efficiencies (81%) than the "as received" electrode due to the reduction of HER. Higher voltage efficiencies (84%) were found at elevated temperatures irrespective of charging time or the modification method. The highest energy efficiency was 65% at 40 °C and 600 rpm for the modified electrode treated with the highest concentration of indium (0.2 mol L^{-1}) and longest dipping period (5 h). Scanning electron microscopy showed no signs of dendritic growth but confirmed the formation of spikes and clusters. Energy dispersive X-ray spectroscopy of the modified graphite electrodes after 340 galvanic cycles showed that indium was still present at the surface of the electrode suggesting good durability.

1. Introduction

Redox flow battery (RFB) is one of the most viable electricity energy storage (EES) technologies targeted for grid-scale owing to its low operating cost, flexibility and scale-ability. The great advantage of this energy storage system is that the energy density is determined independently of the battery power because it is related to the electrolyte concentration and volume whereas the power output is related to the reactor size. By facilitating the storage of large quantities of energy, this technology can enhance the flexibility of power systems and improve the response to the rising demand in energy.

Various classes of flow battery systems exist including the "classic" RFB in which a solution based redox couple is recycled through each half-cell to a reservoir, a common strategy being to separate the half-cells by an ion exchange membrane in a bipolar plate filter-press reactor. During the last decade, several reviews on RFB systems have appeared in the literature highlighting the growing interest in this field [1–5]. Apart from the classic RFB systems there are other types such as the hybrid RFBs. This type of battery differs from the classic RFB in that at least one redox couple species is not fully soluble, which can be either a metal or a gas. The majority of the hybrid flow batteries are zinc based due to the extensive use of zinc in the battery industry [1,2]. Zinc is deposited on an inert collector during charge and then dissolved back to the electrolyte during discharge. Several factors have been found to affect the zinc deposition such as the electrode substrate, charging method, cell geometry, electrolyte hydrodynamics, electrolyte composition and zinc electrode morphology [6].

The zinc-cerium cell is a new redox flow technology that has been developed in the last decade [7–9]. The advantage that the zinc-cerium flow cell has over other current RFB systems is that the cell voltage is ~2.4 V (*c.f.* 1.35 V for the all-Vanadium RFB [3]) and therefore greater power can be delivered by a single unit. Methanesulfonic acid (MSA) is used as the supporting electrolyte, as it allows zinc electroactive species to dissolve at concentrations larger than 2.0 mol L^{-1}. Furthermore, the solubility of cerium carbonate in MSA is considerably higher than in sulfuric acid [7]. During the charge-discharge cycles of the zinc-cerium flow cell the electrodeposition of zinc (1) takes place at the negative side and the cerium oxidation/reduction (3) at the positive side. However, the MSA environment also allows the occurrence of the hydrogen

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evolution reaction (HER-(2)) during the zinc deposition reaction and the oxygen evolution reaction (OER, (4)) during the cerium oxidation.

$$Zn^{2+} + 2e^- \leftrightarrow Zn_{(s)}\ E^\circ = -0.76\,V\ vs\ S.H.E \quad (1)$$

$$2H^+ + 2e^- \leftrightarrow H_2\ E^\circ = 0.0\,V\ vs\ S.H.E \quad (2)$$

The positive half-cell reaction is:

$$Ce^{3+} \leftrightarrow Ce^{4+} + e^-\ E^\circ = +1.64\,V\ vs\ S.H.E \quad (3)$$

$$2H_2O \leftrightarrow 4H^+ + 4e^- + O_2\ E^\circ = +1.23\,V\ vs\ S.H.E \quad (4)$$

Despite the presence of the parallel reactions, MSA is favoured in this particular application, as it suppresses zinc dendrites and so potential short circuit during zinc electrodeposition is avoided [7]. A detailed description of HER in the zinc deposition/dissolution reaction is given in the review of Walsh on the zinc-cerium RFB system where the problems arising in different types of zinc based systems (zinc-bromine, zinc-nickel cells), electrolytes (acidic and alkaline) and operating conditions (flow velocities) are discussed [6].

In order to control the zinc reaction and suppress the HER during zinc deposition (*i.e* charging of the battery) electrolyte additives are routinely implemented. Another function of the additives is controlling the morphology and appearance of the zinc deposits. Several additives and surfactants have been reported for the zinc electrospinning process including CTABr (Cetyltrimethylammonium bromide), coumarin, 2-butyne-1, 4-diol, urea and gelatine [6,10,11]. Metal compounds such as indium and lead have also been found to increase the hydrogen overpotential [6]. Leung [13] has studied the zinc deposition in MSA on a carbon composite electrode (polyvinyl-ester composite) and found that the presence of $2 \times 10^{-3}\,mol\,L^{-1}$ of indium oxide improved the energy efficiency by ~10%, up to 73%. Similar findings were reported in an electrolytes containing 1.25 M Zn(II) in 1–1.5 $mol\,L^{-1}$ H_2SO_4 using indium oxide as an additive [12]. Carbon-based composites are the material of choice for the negative electrode in the Zn-Ce hybrid RFB system [14,15] as they have the advantages of being low cost, light in weight, chemically and mechanically robust. The materials include composites of polymer binders and conductive particles, such as carbon polymer composites [7,14,15] and polymer-impregnated graphite plates [7,16]. Another recent study by Leung on the zinc methanesulfonate medium [17] reported that the corrosion of zinc and the volume of hydrogen evolved varied with time and depended on the surface state and electrolyte conditions. The addition of indium (acting as an inhibitor) in the zinc methanesulfonate medium decreased the zinc corrosion as well as the HER. However, at longer deposition times (>4 h), the indium deposition was not uniform resulting in continued hydrogen evolution over time.

This paper focuses solely on the negative side of the zinc cerium RFB cell, more precisely on the performance of the indium treated carbon based electrodes with regard to the zinc deposition/dissolution process on a highly zinc containing methansulfonate electrolyte. The zinc concentration in this study was *ca.* 2.5 $mol\,L^{-1}$ in 6.5 $mol\,L^{-1}$ MSA 0.5 $mol\,L^{-1}$ higher than previous studies in the same medium (*viz.* 2 $mol\,L^{-1}$ Zn(II) in 6 $mol\,L^{-1}$ MSA) [2]. A high zinc ion concentration is desirable as it supresses zinc corrosion leading to higher charge efficiencies [7,17], while at the same time further increases the energy density of the battery. Regarding the indium modified electrodes, instead of adding indium to the electrolyte; we modified the graphite electrodes through a dip-coating process with indium chloride (0.1–0.2 $mol\,L^{-1}$ $InCl_3$) followed by heat treatment in air (1 and 5 h dwelling times). The zinc deposition and dissolution reactions on the indium treated graphite electrodes subjected to different conditions (indium concentration and duration of the dipping process (t_{Dwell})) were investigated through cyclic voltammetry, Tafel extrapolation, electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge cycles. The experiments were conducted at two different operating temperatures, 25 and 40 °C.

2. Experimental

2.1. Chemicals and Reagents

The zinc methanesulfonate electrolyte, methanesulfonic acid (99%, International Laboratory USA) and ZnO (99.5%, International Laboratory USA) was prepared by stirring the ZnO in deionized water (Milli-Q deionised water, resistivity 18.2 $M\Omega\,cm^{-1}$) according to the following reaction:

$$ZnO + 2CH_3SO_3H \rightarrow Zn(CH_3SO_3)_2 + H_2O\ \mathrm{R1}$$

The indium solution in which the graphite electrodes were immersed for the dip-coating process was prepared by dissolving $InCl_3$ (98%, Sigma Aldrich) in 1 $mol\,L^{-1}$ HCl (33%, Sigma Aldrich). The conductivity of the methanesulfonate solution was measured by a Mettler-Toledo SevenMulti^{TM} S40 high performance pH/mV/°C Meter and the viscosity by a NDJ-9SB Digital Viscometer (Shenyang Faith Trading Co. Ltd).

2.2. Modification of the graphite electrodes

The properties of the "as received" carbon graphite electrode (Tianjin Aidahengsheng Technology Co., Ltd.) are listed in Table 1. Prior to modification, the surface of the electrodes (having a geometric surface area of 0.55 cm^2) was rinsed with ethanol and dried with a stream of N_2. Then, the samples were immersed in indium solution containing either 0.1 or 0.2 $mol\,L^{-1}$ $InCl_3$. Two dwelling times (t_{Dwell}) were selected for this study, *viz.* 1 and 5 h. The thermal treatment was conducted in a muffle furnace (Lindberg/Blue M Moldatherm 1100 °C, Thermo Fisher Scientific) at a carbonization rate of 5 °C h^{-1} at 500 °C for 5 h. In addition, a heat treated graphite electrode with no indium modification was also prepared for comparison. Table 2 lists all the samples investigated in this study. Care was taken to ensure that the samples did not suffer any damage to the exposed surface.

2.3. Electrochemical characterization

A standard three-electrode configuration was employed with platinum gauze acting as the counter electrode, while the reference electrode was $Hg|Hg_2SO_4|K_2SO_4$ (sat) (CH Instruments) with a standard potential of 0.64 V *vs* S.H.E. The electrolyte was contained in a jacketed cell, which enabled its temperature to be controlled (±2 °C) by a thermostatic water bath (Digital Thermostat Water Bath HH-2, Wincom Ltd.). Cyclic votammograms (CV) and EIS measurements were performed using a ZAHNER-IM6 electrochemical workstation. The charge-discharge

Table 1
Properties of the "as received" graphite electrode used for the negative side of the zinc cerium RFB.

Bulk density, ρ	1.8 $g\,m^{-3}$
Compressive Strength	50 MPa (7252 psi)
Average Particle Size	250–300 mesh (57 μm)
Shore Scleroscope Hardness (SSH)*	40

* The Scleroscope hardness test method is based on the rebound height of a diamond-tipped hammer off the sample's surface after it falls a fixed distance.