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Effect of Mixed Acid Media on the Positive Side of the Hybrid Zinc-Cerium Redox Flow Battery

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ABSTRACT

The electrochemical activity of the $Ce^{3+/4+}$ reaction in the presence of various mixed acid electrolytes containing methanesulfonic acid (MSA) as the base electrolyte along with hydrochloric, nitric and sulfuric acid was investigated as a function of acid concentration and reaction temperature on a Pt disk electrode. Cyclic voltammetry in 0.6 $mol\,L^{-1}$ cerium and 4 $mol\,L^{-1}$ MSA with **0.5 - 1** $mol\,L^{-1}$ **hydrochloric acid** showed that the reversibility and kinetics of the **$Ce^{3+/4+}$ reaction were significantly enhanced compared to that containing MSA only. Higher diffusion coefficients (*D*) and exchange current densities (j_o) were also obtained for the mixed acid media containing sulfuric and nitric acid, but in this case the reversibility of the reaction was not that improved.** Higher concentrations of hydrochloric, nitric and sulfuric acid (>1 $mol\,L^{-1}$) made the oxidation of Ce^{3+} very hard to delineate from the cyclic voltammograms because of the side reactions occurring at such high potentials. The exchange current density (j_o), obtained through polarization resistance and electrochemical impedance spectroscopy measurements (EIS), increased with temperature over the range 25 to 55 °C. The EIS results showed that the solution resistance of the mixed electrolytes is considerably lower than that of the unmixed electrolyte facilitating the charge transfer reaction. Nonetheless, solubility issues arose at high Ce^{4+} concentrations (state of charge > 60%) and elevated temperatures (>40 °C).

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1. Introduction

Redox flow batteries (RFB) represent a class of electrochemical energy storage systems in which the active materials of the battery, in both charged and discharged state are soluble and stored externally to the battery system itself. Thus the energy of the redox battery can be determined independently of the battery power as energy relates to the electrolyte volume and concentration whereas power relates to the electrode size, the reactions involved and of course the cell design. In common operation, the charged reactants are circulated through a cell stack, consisting of the electrodes and/or separators, causing spontaneous discharge of the reactive species at the anode and the cathode. Several systems have been examined over the last two decades indicating a growing interest over this specific area for energy storage. These systems include the all-vanadium [1–3], the bromine-polysulfide [4], the iron-chromium [5], the vanadium-bromine [6], the soluble lead-acid [7] and cadmium-chloranil [8] systems. The zinc-cerium cell is a relatively new redox flow technology that has been developing over the past decade or so [9–12]. Its great advantage is its high open circuit cell voltage ($E^{\circ}_{cell} = -2.2$ V compared with 1.4 V for the all-vanadium battery). This high cell potential has naturally a direct impact on the amount of power that can be delivered at a specified current density. The total amount of energy storage of a RFB system is determined by the concentration and volume of the active species dissolved in an electrolyte. For the Zn-Ce system, methanesulfonic acid (MSA) is used as the supporting common electrolyte, as it allows zinc species to dissolve at concentration larger than 2.0 $mol\,L^{-1}$. This is partly due to the fact that ZnO solubility in MSA is ten times greater than in sulfuric acid [13]. The use of this organic acid as the background electrolyte is sustainable as it is less harmful to the environment than other acids commonly used in flow batteries such as sulfuric acid due to its low vapour pressure, absence of volatile organic compounds, low oxygen demand for degradation. For the positive side of the battery, MSA can dissolve cerium carbonate at concentrations larger than 0.7 $mol\,L^{-1}$. The energy density of the system is reported to be between 20 and 37.5 Wh L^{-1} [14]. However, it is very difficult to obtain a higher concentration of cerium species as it has been reported that at temperatures higher than 50 °C the cerium containing electrolyte forms a precipitate due to the formation of either the cerous-ceric hydroxysulfate or ceric sulfate complexes [13]. Furthermore, as a

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result of the high standard potential of the $Ce^{3+/4+}$ couple (1.44 V vs S.H.E), the electron transfer reaction inevitably occurs on the oxidized metal catalyst surface rather than on the pristine metal [14]. A recent study on the electrochemical behavior of the $Ce^{3+/4+}$ reaction revealed that the addition of ligands, such as oxyacids, neutral nitrogen bases, crown ether and acetylacetonate ligands, can stabilize the high oxidation-state cerium [15]. However, it was also reported that the potential of the cerium redox couple is highly sensitive to its ligand environment.

The introduction of mixed acid media has been implemented in the all-vanadium battery to enable extension of the operating temperature range (hence expanding the practical applications of the battery), the energy density, the kinetics as well as the stability of the electrolyte [16]. For the Zn-Ce system, a study on the effect of sulfuric acid on the $Ce^{3+/4+}$ couple has been positive as larger diffusion coefficients, exchange current density as well as rate constant were found in the case of mixed acid media (*eg.* 2 mol L^{-1} CH_3SO_3H, 0.25 - 0.75 mol L^{-1} H_2SO_4 and 0.4 mol L^{-1} Ce). Furthermore, previous studies in 0.6 mol L^{-1} Ce^{3+} and 4.5 mol L^{-1} methanesulfonic acid on a variety of carbon composite substrates as well as Pt and Pt-Ir coatings have showed that better electrochemical performances can be obtained from the carbon composite electrodes but a deterioration of these electrodes was evident [12,14]. This was brought about by the very positive potential of the Ce^{3+}/Ce^{4+} redox reaction and as the high acid concentration [12,14]. Better reversibility and enhanced kinetics were observed at 60 °C, for all the electrodes investigated. The highest exchange current densities (j_o) were achieved at 60 °C for the Pt-Ir based electrodes.

In this study the introduction of mixed acid media (CH_3SO_3H with H_2SO_4, HCl and HNO_3) for the positive side of the zinc-cerium redox flow cell is investigated on a Pt disk electrode with the overall cerium concentration kept at 0.6 mol L^{-1}. Cyclic voltammetry, polarisation resistance and electrochemical impedance spectroscopy (EIS) were employed to evaluate the kinetics of the $Ce^{3+/4+}$ reaction as well as the stability of the electrolyte at three different temperatures (25, 40 and 55 °C).

2. Experimental

A standard 3-electrode configuration was employed, with a platinum wire (CH Instruments) acting as the counter electrode and $Hg|Hg_2SO_4|K_2SO_4$ (sat.) as the reference electrode, which has a potential of 0.64 V *vs S.H.E*. The electrolyte was contained in a jacketed cell which enables its temperature to be controlled (±1 °C) by means of a thermostatic water bath. The electrolyte conductivities were measured by a Mettler-Toledo SevenMulti^{TM} S40 high performance pH/mV/°C Meter. All solutions were prepared using Milli-Q deionised water (resistivity: 18.2 MΩ cm), MSA (99%, International Laboratory USA), sulfuric acid (95-97%, Sigma Aldrich), nitric acid (99%, International Laboratory USA), hydrochloric acid (37%, Sigma Aldrich) and cerium carbonate (99.9% REO, International Laboratory USA). The Ce^{4+} concentration was monitored by colorimetric redox titration [17]. The indicator used to evaluate the Ce^{4+} concentrations, was a 1:10 phenanthroline-ferrous-sulfate complex solution, titrated against standard ferrous ammonium sulfate (International Lab USA) according to Eq. (1)

$$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+} \tag{1}$$

The 1:10 phenonthroline-ferrous sulphate complex was prepared by adding 1:10 phenonthroline hydrate (International Lab USA) and iron sulphate (International Lab USA) to 1 mol L^{-1} of H_2SO_4 (95-97%, Sigma Aldrich). The Pt disk electrode (CH Instruments, electrical conductivity: 1×10^5 S cm^{-1}) was mechanically polished with alumina powder (Purity: >99%, d_{50}: 0.5∼0.7 um, Tianjin Aidahengsheng Technology CO. Ltd.) prior to conduction of the trials. The cyclic votammograms, polarisation resistance and electrochemical impedance spectroscopy (EIS) were conducted using a ZAHNER-IM6 electrochemical workstation controlled by Thales software. For the EIS measurements, in order to fit the data the appropriate circuit was constructed with the aid of SIM software (Simulation and fitting, EIS, Thales software).

Table 1
List of electrolytes employed in the study along with their acid strength [45].

0.6 M $Ce_2(CO_3)_3$ 2 H_2O			
Base electrolyte	Mixed acid electrolyte	Acid	pKa
4 M CH_3SO_3H	-	CH_3SO_3H	−1.92
4 M CH_3SO_3H	0.5 - 2 M H_2SO_4	H_2SO_4	−3*
3 M CH_3SO_3H	+ 1 M H_2SO_4	HNO_3	−1.64
4 M CH_3SO_3H	+ 0.5 - 1 M HNO_3	HCl	−6.3
4 M CH_3SO_3H	+ 0.5 - 2 M HCl		
3 M CH_3SO_3H	+ 1 M HCl		

* First dissociation only

3. Results and Discussion

3.1. Cyclic voltammetry

3.1.1. Hydrochloric acid

Table 1 shows the different mixed acid electrolytes investigated in this study. The supporting electrolyte is MSA as it has previously been reported that hydrochloric acid and nitric acid are not suitable as base electrolytes for this reaction due to the oxidation of Cl^- and the reduction of $NO_3{}^-$ [18]. In addition, the solubility of cerium in sulfuric acid is considerably lower as stated in the experimental section.

Cyclic voltammograms carried out at 25 °C in a solution containing 0.6 mol L^{-1} Ce^{3+} carbonate dissolved in 4 mol L^{-1} MSA and 0.5-1 mol L^{-1} HCl are shown in Fig. 1A. The voltammograms show the effect of hydrochloric acid on the reversibility of the $Ce^{3+/4+}$ reaction using a standard Pt disk electrode. It is clear that the solutions containing hydrochloric acid displayed higher reversibility as well as higher reduction peak current densities than the solution containing MSA only. The anodic-cathodic peak separations of Fig. 1A were 0.67 mV (very close to the ideal value of 60 mV) while the ΔE_p was 0.1 V. The improvement in the reversibility is due to oxidation reaction as its peak shifted 0.5 mV more negative, towards zero.

Similar reversible behavior has been reported in a previous study in a medium containing 0.8 mol L^{-1} Ce and 6.9 mol L^{-1} MSA on various carbon composite electrodes but at temperatures higher than 25 °C [12]. It has been reported that higher temperatures increase the kinetics and reversibility of the cerium reaction on a Pt composite electrode [13] which is in good agreement with the results on the mixed MSA/HCl acid media. Nonetheless, from Fig. 1B it can be seen that the effect of elevated temperature for the oxidation reaction is relatively small (shift of 0.05 mV) and somewhat more significant for the reduction reaction (shift of 0.105 mV) in a solution containing 0.6 mol L^{-1} cerium(III) carbonate dissolved in 4 mol L^{-1} MSA and 1 mol L^{-1} HCl. The latter electrolyte showed the highest cathodic peak current density of 1.61×10^{-1} A cm^{-2}, over four times higher than that of the unmixed electrolyte, *i.e.* 3.4×10^{-2} A cm^{-2} *vs* $Hg|Hg_2SO_4|K_2SO_4$ (sat.).

Fig. 2A shows the cyclic voltammograms of the $Ce^{3+/4+}$ oxidation and reduction reaction in 0.6 mol L^{-1} Ce^{3+} and 4 mol L^{-1} methanesulfonic acid along with 0.5 mol L^{-1} hydrochloric acid. The voltammograms were scanned between 0.0 to 1.95 V at 25 °C. As seen from Figs. 2B and 2C, the oxidation and reduction peak current densities increased linearly with the square root of the potential sweep rate indicating that the reactions were indeed diffusion controlled following the Randles-Sevcik equation principle [19]. The calculated diffusion coefficients (D) for the ceric

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