Impact of electrolyte composition on the performance of the zinc—cerium redox flow battery system

Georgios Nikiforidis, Léonard Berlouis, David Hall, David Hodgson

HIGHLIGHTS

- High output voltage of Zn—Ce redox flow battery.
- High coulombic efficiency (~90%), independent of charging period (10 min–2 h).
- Carbon polymer composite negative electrode materials (PVE and PVDF) stable to repeated cycling.
- High energy efficiency achieved (~64%) at charge/discharge current of 1 A.

ABSTRACT

The zinc—cerium redox flow battery has the highest open circuit cell voltage ($E_{cell} = 2.4$ V) of all the common redox flow battery (RFB) systems being investigated. In this paper, carbon polymer composite materials based on polyvinyl ester and polyvinylidene difluoride are investigated as the negative electrode for this RFB system. Electrolyte composition, particularly on the negative side, is found to play a key role in maintaining high (~90%) coulombic efficiencies for the different charge durations, from 10 min to 4 h, examined. Energy efficiencies >60% are obtained for temperatures in the range 45–55 °C when the zinc ion concentration in the methanesulfonic acid electrolyte is 2.5 mol dm$^{-3}$. No dependence of the energy efficiency on the flow velocity is found, over the range 7.5 cm s$^{-1}$–13.5 cm$^{-1}$.

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1. Introduction

The rapidly growing demand of energy generated by renewable energy sources has given rise to massive market opportunities for redox flow batteries. Redox energy storage systems possess features such as flexible design, long life, simplicity, safety and high reliability with acceptable operation and maintenance costs which is really important in the competitive electricity market. The production of energy on site could reduce burdens on electricity distribution systems and promote the widespread use of renewable and cleaner energy.

Early research on the redox flow batteries (RFBs) was carried out in the 1970’s by the National Aeronautics and Space Administration (NASA) [1], the Energy Development Associates (EDA) [2], as well as several Japanese research institutions [3] on systems which included the Fe/Cr, Fe/Ti [4] and Ru(bpy)$_3$/[BF$_4$]$^2$ [6] couples. During the 1980’s the all-vanadium redox system was developed by Skyllas-Kazacos et al. [7,8]. The success of the all vanadium RFB has also led to the development of the vanadium—cerium [9], the vanadium—polyhalide [10,11], the vanadium—manganese [12] and the vanadium—acetylacetonate [13] systems as they can provide higher cell potentials and energy densities. Over the last decade, a variety of new RFB’s have been developed, such as the soluble lead-acid [14,15], the cadmium—chloranil [16], the bromine—polysulfide [17] the all uranium [18], the all neptunium [19] and the copper—lead dioxide [19] systems. Several hybrid flow batteries have also been developed namely the zinc—bromine [20], zinc—cerium [21], zinc—nickel [22], zinc—chlorine [23] and zinc—air [24] batteries. The majority of the hybrid flow batteries are zinc based due to the extensive use of zinc in the battery industry.

The zinc—cerium RFB has been under development since the early 1990’s by Electrochemical Design Associates Inc. [25,26].
Further investigation of this system was conducted by Plurion Ltd., the University of Southampton [27] and the University of Strathclyde [28]. Its great advantage is its power to weight ratio due to its high open circuit cell voltage ($E_{cell} = 2.4$ V). This high cell potential (cf. 1.4 V for the all-vanadium battery open circuit voltage) has naturally a direct impact on the amount of power that can be delivered at a specified current density. Methanesulfonic acid (MSA) was used as the supporting electrolyte in the hybrid $Zn$–Ce RFB, as it allows the zinc and cerium electroactive species to dissolve at concentrations larger than 2.0 mol dm$^{-3}$ and 8.0 $\times$ 10$^{-4}$ mol dm$^{-3}$ respectively. The cerium salt used was cerium (III) carbonate and its solubility in methanesulfonic acid is about 10 times greater than in sulphuric acid [29,30]. Spotnitz et al. [31] have reported that the solubility of Ce(IV) increases at high methanesulfonic acid concentrations but the reverse is true for the Ce(III) species. The effect of the acid concentration on the Ce(IV)/Ce(III) species has been also discussed by Raju et al. [32], Leung et al. [33] and Paulenova et al. [34]. In the long term, the use of this organic acid as the background electrolyte is sustainable as it is less harmful to the environment than other acids such as sulphuric acid used in flow batteries due to its low vapour pressure, absence of volatile organic compounds, low oxygen demand for degradation and its low toxicological risk potential viz. LD$_{50}$ = 1000 mg kg$^{-1}$ [35]. It is odourless, chemically stable and free of nitrogen, phosphorous and halogens.

The flow cell in its basic form consists of a single anode–cathode pair with a cation exchange membrane separating the anode and the cathode. In the uncharged state, the zinc electrolyte and the cerium (III) electrolyte are stored externally in separate reservoirs and are circulated during the operation of the battery. For the negative side of the flow battery, the primary reaction is the zinc deposition/dissolution reaction. The methanesulfonic acid environment could also give rise to the hydrogen evolution reaction (HER) during the zinc deposition reaction but the HER becomes kinetically inhibited once zinc is present on the electrode surface as the exchange current density ($i_0$) for hydrogen evolution reaction on zinc is some seven orders of magnitude lower than it is on Pt. In the charged state, the electrodeposited zinc active material is stored within the electrochemical cell on the negative electrode.

At the positive electrode of the zinc–cerium flow battery, the primary reaction during charge is the oxidation of the Ce(III) to form Ce(IV). Due to the high standard potential of the Ce(III)/Ce(IV) couple, viz. 1.44 V vs SHE, the electron transfer reaction is inevitably accompanied by the aqueous solvent breakdown resulting in oxygen evolution at the anode. This situation is not helped by the fact that few electrode materials can withstand this high oxidation potential over prolonged periods which means that metal (oxide) coatings, such as the Pt/Ir on a titanium base, present the most stable materials currently available for the positive electrode. Unfortunately, these tend to also be good O$_2$ evolution catalysts.

The reactions of the zinc–cerium flow cell during discharge are:

$$Zn \rightarrow Zn^{2+} + 2e^-$$
$$2Ce^{3+} + 2e^- \rightarrow 2Ce^{4+} \quad E^0 = 2.40 \text{ V}$$

which indicates the dissolution of the zinc and the reduction of the Ce(IV) to yield the metal methanesulfonate complexes in the solution. In this study, the characterisation of the zinc electrodeposits on the carbon composite electrode materials are first reported prior to the incorporation of the composite electrodes into the flow cell where investigations of their performance in this system were conducted. The effect of other parameters, such as the electrolyte composition (different zinc and methanesulfonic acid concentrations), temperature and flow velocity on the energy efficiency ($\eta$) during charge–discharge cycles are also investigated.

2. Experimental

In the electrochemical studies to examine the nucleation and growth of the zinc electrodeposits, the carbon polymer composite materials were cut into cylinders of suitable diameter (7 mm), which could be mounted using electrically conducting paint (silver conducting paint (RS 186–36000)) onto an Oxford Electrodes$^{(5)}$ rotating disc electrode holder. The materials were sealed with a glue resin (Loctite 3430A + B Hysol$^{(6)}$) so as to prevent any contact of the solution to the support. The surface of the carbon composites was rinsed with ethanol prior to use and dried in an air stream. Care was taken to ensure that the exposed surface of the samples did not suffer any mechanical damage. The physical characteristics of the carbon composite samples examined are given in Table 1.

The flow battery experiments were carried out using a system/apparatus, similar to that described in the paper of Leung et al. [27]. The cell was constructed from HDPE with dimensions of 190 mm $\times$ 265 mm. Flow channels were designed into the cell to direct the flow over the electrodes. The exposed geometric areas of both positive and negative working electrodes were 10 cm $\times$ 10 cm. A 117 Nafion$^{(8)}$ membrane was used as a separator between the anode and cathode compartments in the cell (thickness = 175 $\mu$m, Dupont$^{(8)}$) [36]. Membrane-electrode spacings were adjusted through the use of silicone rubber gaskets to yield hydraulic diameters of the order of 1.8 cm. A peristaltic pump (Masterflex$^{(8)}$) was employed to flow the solutions into and out of the flow cell with the aid of Masterflex$^{(8)}$ precision tubing. Typical Reynolds numbers achieved with the flow cell were in the range 25–172. Two 500 mL amber packer jars (FisherBrand) with a Teflon face lined cap were used as reservoirs for the flow cell. These were placed in a thermostated water bath with the operating temperature controlled by a Gallenkamp thermostirrer 95. All solutions were prepared using Milli-Q deionised water (resistivity 18.2 M$\Omega$ cm) using methanesulfonic acid (70%, BASF), ZnO (99.5%, Fisher Chemicals) cerium (III) carbonate (Sigma Aldrich or Zibo Jiahua Advanced Material Resources Co. Ltd.). The two carbon composite materials tested on the negative side of the flow cell were the PVE (polyvinyl ester) [37] and the PVDF (polyvinylidene difluoride) based [38] electrodes (Table 1). A detailed study on the effect of vinyl ester resins on expanded graphite have been given by Fu et al. [39] while the electrical properties of the polyvinylidene difluoride were investigated by Cunningham et al. [40], Del Rio et al. [41] and Chunhui et al. [42]. The materials were mounted onto a titanium base plate using silver conductive paint (RS 186-36000) and araldite (Loctite 3430A + B, Hysol$^{(6)}$) was used to seal the mounted electrode and expose only the desired surface area. For the positive side, a 10 cm $\times$ 10 cm plated titanium mesh (10 g m$^{-2}$ Pt) was employed. The charge–discharge cycles were carried out using an EG & G M100A Potentiostat/Galvanostat controlled by custom written software in LabVIEW. The reference electrode employed for

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Carbon polymer composite materials used for the negative side of the zinc cerium RFB</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVE</td>
<td>Polyvinyl ester: 3–5 mm thickness</td>
</tr>
<tr>
<td></td>
<td>Thermal conductivity through plane: 18.5 W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Specific heat through plane: 8 $\times$ 10$^{-3}$ J g$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene difluoride: 3–5 mm thickness</td>
</tr>
<tr>
<td></td>
<td>Thermal conductivity through plane: 20 W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Permeability coefficient: 10$^{-5}$ cm$^{2}$ s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Bulk density: 2.1 g m$^{-3}$</td>
</tr>
</tbody>
</table>


the three-electrode cell measurements was a K₂SO₄ saturated Hg/Hg₂SO₄ electrode which has a potential of 0.64 V vs. the standard hydrogen electrode. The Ce(IV) concentration in the flow cell reservoir following charging was measured by titration against standardised ferrous ammonium sulphate solution with a phenanthroline–ferrous sulphate complex as a colorimetric redox indicator. The total cerium content of the solutions was determined by inductively coupled plasma mass spectrometry (Agilent Technologies 7700 ICPMS Series).

3. Results and discussion

3.1. Zinc deposition reaction

Fig. 1 shows the cyclic voltammogram recorded at 60 °C in a solution containing 1.5 mol dm⁻³ zinc methanesulfonate electrolyte in 2.7 mol dm⁻³ MSA. In the initial measurement, the potential sweep (scan rate = 20 mV s⁻¹) was reversed when the potential reached a value of −1.8 V vs. Hg/Hg₂SO₄/K₂SO₄ (sat.) for the PVE carbon composite electrode. It can be seen that on the forward sweep, a sharp rise in the current occurs just beyond −1.5 V and no peak is observed to the limit of −1.8 V. As the figure indicates, extending this limit to −2.0 V still leads to no diffusion peak and this is due to the high concentration of the zinc ions present (mass transport limiting current density $i_L \sim 3$ A cm⁻²). The nucleation loop verifies the formation of a new metal phase on the forward sweep and on the reverse sweep, rapid dissolution occurs at potentials beyond −1.4 V, giving a peaked response at the maximum rate of anodic dissolution. The difference between the two stripping curves in the figure is simply due to the different amounts of zinc deposited on the forward negative scan.

By carrying out potential step studies close to the start region of the sharp current increase on the forward sweep, the nature of the nucleation process and growth of the zinc electrodeposits could be examined. Fig. 2 shows the normalised current–time response, with respect to the time $t_m$ to the current maximum $I_m$ [43], for zinc deposition using the above noted solution at a potential of −1.47 V. The initial fall in the data is due to double layer charging current and this is followed by a rise and then fall in the current due to nucleation, growth and overlapping of the zinc nuclei. Superimposed onto the experimental data are the corresponding simulated curves for instantaneous and progressive nucleations based on the work by Scharifker et al. [43] and it is clear that on the PVE surface under these experimental conditions, the instantaneous process, whereby all nuclei are formed simultaneously, is favoured.

As indicated in Table 2, the nuclei density $N_e$ evaluated from these profiles increase as the applied potential is made more negative and this is consistent with more energy being available to form the nuclei. The large nuclei densities recorded here on the PVE electrode are similar to those reported for zinc on other carbon composite electrodes and are consistent with the high concentration of the zinc ions present in this solution. It is also worth mentioning that in the nucleation data at the more negative potentials (e.g. as in Ref. [28]), the falling transient expected at longer times did not occur due to the presence of the accompanying HER.

Naturally, one of the key issues to be addressed with any material to be employed as the negative electrode in the flow battery system is how well the carbon composites can withstand repeated charge/discharge cycles under the high methanesulfonic acid concentrations (~1.5 M) and temperatures (35 °C–55 °C) for the process. Figs. 3 and 4 show the microscopic pictures of the surfaces of the PVDF and PVE electrodes respectively, prior to and after over 40 charge/discharge cycles were carried out at a current density of 50 mA cm⁻² using the rotating disc set-up at 60 °C. The initial electrode surfaces ($\phi = 7$ mm), particularly for the PVE, exhibited a slightly mottled appearance whereas that of the PVDF electrode appeared much smoother. However, no significant deterioration or loss of integrity of either electrode surface was observed (Figs. 3(b) and 4(b)) following these galvanic cycling and the coulombic efficiency too remained unaffected over these cycles. Indeed, electrode degradation under the above conditions did not manifest itself on these two composite carbon materials until a number of cycles were in the region of ~200. Then, a decrease in both the current and the voltage efficiencies as well as an increase in electrode roughness were observed. The change in the morphology of the PVE surface is revealed by the SEM micrographs of Fig. 5(a–d) which shows the loss in the integrity of

![Fig. 1. Cyclic voltammograms at a PVE electrode in 1.5 mol dm⁻³ Zn(II) and 2.7 mol dm⁻³ CH₃SO₃H. Scan rate 20 mV s⁻¹; temperature 60 °C. Negative limits of −1.8 V (blue curve) and −2.0 V (red curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)

![Fig. 2. Normalised $I_m$ vs $t_m$ curve for the nucleation of zinc on a PVE electrode at a potential of −1.47 V in a solution contacting 1.5 mol dm⁻³ Zn(II) in 2.7 mol dm⁻³ CH₃SO₃H. Simulated curves for instantaneous and progressive nucleations are also shown.](image)

<table>
<thead>
<tr>
<th>Potential/V</th>
<th>$N_e \times 10^6$ cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>−1.460</td>
<td>0.501</td>
</tr>
<tr>
<td>−1.470</td>
<td>0.888</td>
</tr>
<tr>
<td>−1.480</td>
<td>1.41</td>
</tr>
<tr>
<td>−1.490</td>
<td>1.64</td>
</tr>
<tr>
<td>−1.495</td>
<td>1.78</td>
</tr>
<tr>
<td>−1.500</td>
<td>2.07</td>
</tr>
<tr>
<td>−1.510</td>
<td>2.22</td>
</tr>
</tbody>
</table>
the composite layer as a result of the increased number of galvanic cycles. Even on the lowest magnification (~9.8×), the change in the surface of the PVE electrode from an essentially smooth (Fig. 5(a)) to a roughened texture is clearly evident (Fig. 5(c)) following the galvanic cycling experiments. The finer details of that surface are revealed in the micrograph of Fig. 5(d) in which features as large as ~200 μm in length are observed on the roughened electrode surface. This surface texture of the carbon polymer composite could explain the poor adhesion of the zinc deposits leading to the low coulombic efficiencies found in the latter stages of these galvanic cycles.

The rotating disc electrode set-up was also quite useful in providing samples which allowed the morphology of the zinc deposits on these carbon composite electrode substrates to be readily assessed. The data in Fig. 6 shows the SEM micrographs of zinc deposits following a 40 min deposition on the PVDF electrode from a 1.5 M Zn²⁺ solution in 2.7 M MSA at 60 °C and a rotation rate of 10 Hz. The lower magnification picture (44×) shows a generally smooth surface but peppered with small (~10–20 μm diameter) pinholes over the surface. This suggests that hydrogen evolution on the original bare carbon substrate, prior to the start of the electrodeposition of the zinc, had prevented the adhesion of the zinc deposits at these points. These pinholes, although numerous, formed only a very small part of the zinc electrodeposited surface layer and so did not adversely affect the coulombic efficiency of the zinc deposition/dissolution process, as is discussed below. The more detailed micrograph of the deposits shown in Fig. 6(b) reveals an assembly of intertwined plate-like features but no evidence of dendritic growth.

3.2. Cerium half cell reaction

The cerium redox reaction in the MSA electrolyte and in mixed MSA-H₂SO₄ media [44] has been extensively studied on a variety of substrates ranging from carbon–polymer composites and high surface area carbon felts to platinised-titanium meshes [9,33,45]. These have met with various successes over long term charge/discharge cycles and operation at high current densities [33] with the Pt–Ti mesh and the SGL carbon felt electrodes exhibiting the best performance. In the present study, a 10 cm × 10 cm Pt–Ti mesh welded onto a Pt–Ti plate was used as the positive electrode for all the flow cell studies. Fig. 7 shows the ‘stabilised’ cyclic voltammograms obtained at 25 °C, 40 °C and 60 °C for this substrate in a solution containing 8.0 × 10⁻² mol dm⁻³ Ce(IV) and 7.2 × 10⁻¹ mol dm⁻³ Ce(III) in 4.4 mol dm⁻³ MSA. The Ce(III) oxidation peak is clearly visible at ca. 1.1 V followed by the oxygen evolution reaction beyond 1.2 V vs. Hg/Hg₂SO₄/K₂SO₄(sat.). There is very little dependence of the peak potential on temperature although there is a substantial increase in the peak current density with temperature. For the Ce(IV) reduction reaction however, there is a significant change in both peak potential and current density. The reversibility of the reaction is facilitated at elevated temperatures (ΔEₚ₋ₚ = 290 mV and 240 mV at 25 °C and 60 °C respectively) and the increase in the current density can be readily attributed to a
decrease in the viscosity of the solution and so increase in diffusion coefficient with increasing temperature. The narrower peak separation ($\Delta E_{p-p} = 707$ mV from Ref. [33]) for the reaction obtained at the Pt–Ti mesh indicates that it performed better than the Pt electrode used in that study. Furthermore, as can be seen from Fig. 7, the ratio of the cathodic to anodic peak is much closer to unity than the value of 0.53 obtained by these authors [33].

3.3. Zinc cerium flow cell

A number of different electrolyte compositions, shown in Table 3, were tested in the zinc cerium flow cell. The rationale here, at least for the negative side, was to evaluate the impact of any concentration polarisation effects of the zinc ions during the charging (deposition) stage of the process. The composition of the positive electrolyte was the same for all the electrolytes, viz. $5.9 \times 10^{-1}$ mol dm$^{-3}$ Ce(IV), $8.0 \times 10^{-2}$ mol dm$^{-3}$ Ce(III), $8.0 \times 10^{-1}$ mol dm$^{-3}$ Zn(II), and $3.5$ mol dm$^{-3}$ excess MSA. The presence of zinc ions on the positive side serves to reduce the mass transfer losses from the negative electrolyte across the membrane. In the latter electrolyte, the zinc concentration ranged from $1.5$ mol dm$^{-3}$ to $2.5$ mol dm$^{-3}$. The effectiveness of these electrolytes was investigated in terms of the coulombic ($\eta_C$) and voltage efficiencies ($\eta_V$) for various charging times ranging from 1 min to 4 h at charging/discharging current densities of 10 mA cm$^{-2}$. Other operating conditions that were examined were temperature and electrolyte flow rate. In the case of the latter, the flow velocities employed were between 7.5 cm s$^{-1}$ and 13.5 cm s$^{-1}$ (i.e. well within...
the laminar flow range) but as Table 4 indicates, there was very little variation in ηC and ηV observed within this flow regime.

The direct impact of the zinc ion concentration on the coulombic efficiency ηC can be seen from the data of Fig. 8, obtained using a PVE working electrode out with the flow cell in a 3-electrode arrangement with a 5 min charge at 50 mA cm$^{-2}$ and a temperature of 60 °C. It is clear that ηC values in excess of 95% were obtained when the Zn$^{2+}$ ion concentration was greater than 1.5 mol dm$^{-3}$. Note that here as the zinc concentration in the electrolyte was increased but the total acid concentration remained the same, an effective decrease in the excess MSA concentration resulted. According to Leung et al. [46], lower methanesulfonic acid concentrations would lead to higher coulombic efficiencies under these conditions did not lead to any increase in the resistance of the electrodeposition or in overpotential losses.

The effect of the different carbon composite materials on ηC and ηV for the zinc deposition reaction in a 3-electrode arrangement has already been discussed in a previous paper [28] where the PVDF carbon composite working electrode showed good performance in terms of ηC (~96%), robustness and cycling stability (>200 charge discharge cycles). The data summarised in Table 6 was obtained from the PVE electrode in a flow cell arrangement. This showed a fall in the coulombic efficiency with increasing charge time but again here, no change in the voltage efficiency was observed over the three temperatures examined. There was however a significant fall in the coulombic efficiency measured at 35 °C with increasing charge time indicating that the electrode kinetics for the redox reactions are poorly optimised at this lower temperature.

A further increase in zinc ion concentration to 2.5 mol dm$^{-3}$ with an excess MSA concentration of only 1.5 mol dm$^{-3}$ resulted in the charge/discharge curves shown in Fig. 10. Here, 20 cycles were conducted with a 30 min charge period at a current density of 10 mA cm$^{-2}$. The discharge voltage shows some fluctuation but remains above 2.0 V until the sharp fall at the end of the discharge.

Table 4
Impact of flow velocity on the coulombic and voltage efficiencies for the PVDF electrode in the flow cell following a 5 min charge in Electrolyte 1 at a temperature of 45 °C.

<table>
<thead>
<tr>
<th>Flow velocity/cm s$^{-1}$</th>
<th>ηC</th>
<th>ηV</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>89%</td>
<td>60%</td>
</tr>
<tr>
<td>9.0</td>
<td>91%</td>
<td>61%</td>
</tr>
<tr>
<td>10.5</td>
<td>90%</td>
<td>59%</td>
</tr>
<tr>
<td>12.0</td>
<td>90%</td>
<td>60%</td>
</tr>
<tr>
<td>13.5</td>
<td>89%</td>
<td>59%</td>
</tr>
</tbody>
</table>

Fig. 7. Stabilised cyclic voltammograms showing the effect of temperature on the Ce(IV)/Ce(III) couple at a Pt–Ti mesh electrode in a solution containing 8.0 × 10$^{-2}$ mol dm$^{-3}$ Ce(IV) and 7.2 × 10$^{-3}$ mol dm$^{-3}$ Ce(III) in 4.4 mol dm$^{-3}$ CH$_3$SO$_3$H. Scan rate 40 mV s$^{-1}$.

Fig. 9 shows ten charge/discharge cycles carried out in the flow cell using the PVDF electrode, in a 2.0 mol dm$^{-3}$ Zn$^{2+}$ solution and 1.7 mol dm$^{-3}$ excess MSA at a temperature of 45 °C. The charging current here was 10 mA cm$^{-2}$ and was applied for 1 h. It is obvious from the data that the coulombic efficiency under these conditions is considerably less than that of the 90%+ value reported above. Furthermore, from the data in Table 5 for this system, there is also a strong dependence of the coulombic efficiency on the charging period, with ηC decreasing from to 90% for a 5 min charge to 72% after a 2 h charge at 45 °C. A possible explanation for this could be

Table 3
Composition of various electrolytes used in the study of the zinc cerium RFB.

<table>
<thead>
<tr>
<th>Concentration/mol dm$^{-3}$</th>
<th>Electrolyte</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative electrolyte</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce (III)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn(II)</td>
<td>1.50</td>
<td>2.00</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>CH$_3$SO$_3$H (excess)</td>
<td>2.70</td>
<td>1.70</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>Positive electrolyte</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Ce</td>
<td>0.67$^b$</td>
<td>0.67$^b$</td>
<td>0.67$^b$</td>
<td></td>
</tr>
<tr>
<td>Ce (III)</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Ce (IV)</td>
<td>0.59$^a$</td>
<td>0.59$^a$</td>
<td>0.59$^a$</td>
<td></td>
</tr>
<tr>
<td>Zn(II)</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>CH$_3$SO$_3$H (excess)</td>
<td>3.50</td>
<td>3.50</td>
<td>3.50</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Maximum [Ce(IV)] during trials.
$^b$ Concentration determined by ICP-MS.

that at the current density of 10 mA cm$^{-2}$ employed in the flow cell, the deposit surface morphology was different from the plate-like features observed in Fig. 6(b), obtained at the current density of 50 mA cm$^{-2}$ and so gave rise to more dendritic and non-uniform growth, which could be more easily removed from the surface by the flowing solution. The decrease in ηC with increasing charging time could also be tentatively attributed to the hydrogen evolution reaction but this is unlikely since zinc inhibits the HER. The coulombic efficiencies are some 20% lower at the temperature of 55 °C which would suggest that the chemical dissolution (i.e. corrosion) rate of the zinc electrodeposits in this solution is enhanced at this temperature. There is no significant variation in the voltage efficiency between these two temperatures indicating that the nature and morphology of the zinc deposits formed under these conditions did not lead to any increase in the resistance of the electrodeposits or in overpotential losses.

Fig. 8. Effect of zinc ion concentration on ηC for the zinc half–cell reaction measured at a PVE electrode with 5.7 mol dm$^{-3}$ CH$_3$SO$_3$H as the base electrolyte. Electrode rotation rate 10 Hz; temperature 60 °C. Charge current density of –50 mA cm$^{-2}$ for 5 min/ discharge at 50 mA cm$^{-2}$.
The charge–discharge voltage curves on the other hand show a relatively flat profile with an average value of 2.78 V. The full data set obtained from this study is summarised in Table 7. The data in the table indicate that with this increased zinc concentration, operating the PVE electrode at 55 °C and an open circuit voltage of 2.45 V, an overall area–resistance for the redox flow battery can be estimated as 40 Ω cm² using:

\[
\text{Area resistance} \left( \Omega \text{ cm}^2 \right) = \frac{2.45}{0.01} \times \left( 1 - \eta_c \right)
\]

This value is even larger at 45 °C (50 Ω cm²) and at 35 °C (56 Ω cm²). This decrease of 16 Ω cm² in going from 35 °C to 55 °C is more likely to be linked to an improvement in the electrode kinetics of the zinc and cerium reactions with increasing temperature rather than a change in contact resistance. Nevertheless, it is still evident that the main resistance component in the cell does arise from the method of attachment of the carbon polymer composite to the base current collector. There is no doubt that the area resistance will have to be substantially reduced by at least one order of magnitude in

The charge–discharge voltage curves for a PVDF electrode in 2.0 mol dm⁻³ Zn²⁺ solution in 1.7 mol dm⁻³ MSA (Electrolyte 2) at 45 °C. 1 h charge at 10 mA cm⁻² and a flow velocity of 10.5 cm s⁻¹.

Fig. 9. Charge–discharge voltage curves for a PVDF electrode in 2.0 mol dm⁻³ Zn²⁺ solution in 1.7 mol dm⁻³ MSA (Electrolyte 2) at 45 °C. 1 h charge at 10 mA cm⁻² and a flow velocity of 10.5 cm s⁻¹.

Table 5
Effect of charging time and temperature on η_c and η_v in Electrolyte 2 for the PVDF electrode. Flow velocity = 10.5 cm s⁻¹. Current density 10 mA cm⁻².

<table>
<thead>
<tr>
<th>Charge time (minutes)</th>
<th>45 °C</th>
<th>55 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>η_c</td>
<td>η_v</td>
</tr>
<tr>
<td>2</td>
<td>91%</td>
<td>60%</td>
</tr>
<tr>
<td>5</td>
<td>90%</td>
<td>59%</td>
</tr>
<tr>
<td>10</td>
<td>82%</td>
<td>58%</td>
</tr>
<tr>
<td>30</td>
<td>81%</td>
<td>59%</td>
</tr>
<tr>
<td>60</td>
<td>80%</td>
<td>59%</td>
</tr>
<tr>
<td>120</td>
<td>77%</td>
<td>61%</td>
</tr>
<tr>
<td>240</td>
<td>73%</td>
<td>61%</td>
</tr>
</tbody>
</table>

Table 6
Effect of charging time and temperature on η_c and η_v in Electrolyte 2 for the PVE electrode. Flow velocity = 9 cm s⁻¹. Current density 10 mA cm⁻².

<table>
<thead>
<tr>
<th>Charge time (minutes)</th>
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<th>45 °C</th>
<th>55 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>η_c</td>
<td>η_v</td>
<td>η_c</td>
</tr>
<tr>
<td>1</td>
<td>83%</td>
<td>60%</td>
<td>85%</td>
</tr>
<tr>
<td>2</td>
<td>74%</td>
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<td>79%</td>
</tr>
<tr>
<td>5</td>
<td>67%</td>
<td>62%</td>
<td>78%</td>
</tr>
<tr>
<td>10</td>
<td>62%</td>
<td>64%</td>
<td>76%</td>
</tr>
<tr>
<td>30</td>
<td>56%</td>
<td>62%</td>
<td>72%</td>
</tr>
<tr>
<td>60</td>
<td>53%</td>
<td>61%</td>
<td>69%</td>
</tr>
<tr>
<td>120</td>
<td>49%</td>
<td>64%</td>
<td>66%</td>
</tr>
<tr>
<td>240</td>
<td>49%</td>
<td>64%</td>
<td>66%</td>
</tr>
</tbody>
</table>

Table 7
Effect of charging time and temperature on η_c and η_v in Electrolyte 3 for the PVE electrode. Flow velocity 12 cm s⁻¹. Current density 10 mA cm⁻².

<table>
<thead>
<tr>
<th>Charge time (minutes)</th>
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<th>45 °C</th>
<th>55 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>η_c</td>
<td>η_v</td>
<td>η_c</td>
</tr>
<tr>
<td>10</td>
<td>83%</td>
<td>62%</td>
<td>88%</td>
</tr>
<tr>
<td>30</td>
<td>81%</td>
<td>63%</td>
<td>94%</td>
</tr>
<tr>
<td>60</td>
<td>77%</td>
<td>62%</td>
<td>91%</td>
</tr>
<tr>
<td>120</td>
<td>75%</td>
<td>61%</td>
<td>88%</td>
</tr>
</tbody>
</table>

Fig. 10. Charge–discharge voltage curves for a PVE electrode in Electrolyte 3 at 55 °C. 30 min charge at 10 mA cm⁻² and flow velocity of 12 cm s⁻¹.
order for the energy efficiency of the Zn–Ce RFB to become comparable to those of the all-vanadium and Zn–Br2 RFB's at ~80%.

4. Conclusions

The highest coulombic and voltage efficiency values in the flow cell viz. 92% and 70% respectively, were obtained from an electrolyte system consisting of 2.5 mol dm⁻³ Zn(II) in 1.5 mol dm⁻³ CH₃SO₃H on the negative side and 5.9 × 10⁻¹ mol dm⁻³ Ce(IV) 8 × 10⁻¹ mol dm⁻³ Ce(III) in 3.5 mol dm⁻³ CH₃SO₃H on the positive side. Energy efficiency ηe values of 64% and 61% were found for the PVE and PVDF carbon composites respectively, at current densities of 10 mA cm⁻² and charging times between 10 min and 2 h. The optimum operating temperature was 55 °C for the PVE carbon electrode while for the PVDF it was found to be 45 °C. The overall number of cycles conducted with both carbon composite electrodes was 100 and they exhibited good stability and robustness during these cycles. The coulombic efficiency with zinc ion concentrations of 2.5 mol dm⁻³ at temperatures greater than 45 °C was found to be independent of charging duration with ηe values between 85% and 90% being recorded. This was partly attributed to the minimisation of the HER process during the zinc deposition reaction.

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References