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

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#### A R T I C L E I N F O

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#### 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  $7.5 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>. 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  $2 \times 10^{-3}$  mol dm<sup>-3</sup> 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<sup>-2</sup>.

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#### 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, loadlevelling, 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:

$$Zn(II) + 2e^{-} \underset{\text{discharge}}{\stackrel{\text{charge}}{\Rightarrow}} Zn \quad E^{\circ} = -0.76 \, \text{V} \, vs. \, \text{SHE}$$
(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]:

$$Ce(III) - e^{- \underset{\text{discharge}}{\text{charge}}} Ce(IV) \quad E^{\circ} \approx +1.28 - 1.72 \, \text{V} \, vs. \, \text{SHE}$$
(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 2.4V [12]. Recent attention has focused on the application of aqueous methanesulfonic acid as an electrolyte

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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 ( $18 M \Omega cm$  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<sup>3</sup>. 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<sup>2</sup>) while the counter electrode was a large area platinum mesh (projected area: 1 cm<sup>2</sup>). The working and counter electrode compartments were separated by a Nafion<sup>®</sup> membrane (Dupont, NF115/H<sup>+</sup>). The electrode potential was measured against a saturated silver/silver chloride electrode (ABB, Series 1400, 1.0 mol  $dm^{-3}$  KNO<sub>3</sub>). 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<sup>-1</sup>. Cyclic voltammograms were recorded over a wide range of electrolyte composition including 10-80 mmol dm<sup>-3</sup> zinc methanesulfonate in 0.5 mol dm<sup>-3</sup> 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<sup>®</sup> membrane (DuPont, NF117/H<sup>+</sup>) 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  $4.5 \text{ cm} \times 2 \text{ cm} (9 \text{ cm}^2)$  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<sup>3</sup>. Both positive and negative electrolytes were circulated at a mean linear flow velocity between 1.8 and 7.8 cm s<sup>-1</sup> through the cell using a peristaltic pump (Masterflex<sup>®</sup> Model 7553079, Cole-Parmer) with high-pressure tubing (Masterflex<sup>®</sup> Norprene<sup>®</sup>, Cole-Parmer). The negative electrode compartment contained 0.5-2 mol dm<sup>-3</sup> zinc methanesulfonate in 0.5-3 mol dm<sup>-3</sup> methanesulfonic acid while the positive electrode compartment contained 1.0 mol dm<sup>-3</sup> methanesulfonic acid. The temperature of both electrolytes was controlled at  $(293-343) \pm 2$  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  $20-80 \text{ mA cm}^{-2}$  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<sup>-3</sup> KNO<sub>3</sub>) 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  $1.5 \text{ mol dm}^{-3}$  zinc methanesulfonate and  $1 \text{ mol dm}^{-3}$  methanesulfonic acid electrolyte ( $60 \text{ cm}^3$ ) in a  $100 \text{ cm}^3$  glass beaker. The applied current density was  $50 \text{ mA cm}^{-2}$  for 4 h. Carbon polyvinyl-ester composite (Engtegris Inc., BMC 18649, Germany) electrodes of 8 cm  $\times$  1 cm dimensions and with an exposed electrode area of 4 cm  $\times$  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<sup>®</sup> 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.

#### 3. Results and discussion

#### 3.1. Cyclic voltammetry

Fig. 1a shows the cyclic voltammogram of Zn(II) ions using a glassy carbon electrode at  $20 \, \text{mV} \, \text{s}^{-1}$  potential sweep rate in an electrolyte containing  $0.01 \, \text{mol} \, \text{dm}^{-3}$  zinc methanesulfonate and  $0.5 \, \text{mol} \, \text{dm}^{-3}$  sodium methanesulfonate adjusted at pH 4 with methanesulfonic acid at 295 K. The potential was firstly swept from  $-0.8 \, \text{V}$  to  $-1.4 \, \text{V}$  vs. Ag|AgCl.

The voltammogram is similar to those reported in other acid media. The cathodic scan shows the potential at -1.15 V vs. Ag|AgCl, which is comparable to ca. -1.2 V vs. SCE reported in sulfate, chloride and acetate electrolytes [31]. The sharp increase in current reduction was due to the formation of fresh zinc nuclei, and the further increase of the available deposition area. The peak current density reached *ca.* 2.57 mA cm<sup>-2</sup> at -1.22 V vs. Ag|AgCl due to the reaction of Zn(II) ions already on the electrode surface. After the peak, the current density decreased as no more Zn(II) ions were present at the surface and new Zn(II) species had diffused from the bulk of the electrolyte. Since the standard electrode potential of zinc deposition is more negative than hydrogen evolution, hydrogen gas could evolve by the cathodic reduction of hydrogen ions on the newly formed zinc nuclei. Although the cyclic voltammogram does not show the evolution of hydrogen gas, a fraction of the current is probably due to proton reduction. The scan was reversed at -1.4 V vs. Ag|AgCl in order to avoid hydrogen evolution at more negative potentials

While sweeping the potential towards the positive direction, zinc ions were still being reduced until the crossover potential at -1.16 V vs. Ag|AgCl on the foot of the stripping peak. At -1.14 V vs. Ag|AgCl, solid zinc was no longer thermodynamically stable on the electrode surface and the metallic zinc deposited on the electrode oxidizes very quickly as the oxidation process was not diffusion controlled and a sharp high current peak was observed. The forward and reverse scans form a nucleation loop between -1.16 V and -1.18 V vs. Ag|AgCl. The slightly more negative potential during Zn(II) reduction observed during the forward scan shows that the deposition of zinc on the less-conductive glassy carbon substrate required slightly more energy than that on the freshly deposited zinc surface.

In this study, the overpotential for zinc electrodeposition was ca. -20 mV, as the nucleation potential on glassy carbon electrode is more negative than that on metallic electrode. For instance, Gomes and da Silva Pereira [32] reported that the nucleation potential of zinc electrodeposition was observed at ca. -0.8 V vs. SCE at a stainless steel electrode from the sulfate bath in the absence of an electrolytic additive. Such an overpotential was reported to have important implications for the morphology of the deposit and the current efficiency. Volmer and Weber [33] suggested that a larger overpotential could lead to faster nucleation rate and prevent further grain growth [33–37], which has been reviewed by Budevski et al. [38]. Finer grain size and sometimes more uniform deposits have been obtained at larger deposition overportentials, which was found to be largely dependent on anions molecules [31,39,40], electrolytic additives [36,41,42], temperature [31,43] and the influence of pH on the formation of zinc complexes [44,45]. As suggested by Morón et al. [46], the crystal size of zinc deposit was also influenced by the exchange current density. Due to the reduced exchange current density induced by the adsorption of electrolytic additives on the electrode surface, compact and reflective coatings have been obtained from an acid chloride bath.

In terms of electron transfer, the zinc deposition reaction in a methanesulfonate bath is considered to be a quasi-reversible reaction, as the separation of peak potentials was 160 mV. Literature reports show that the separation of peak potentials for the Zn(II)/Zn(0) reaction in chloride and sulfate electrolytes was *ca.* 100 mV and 150 mV, respectively, in an electrolyte containing 0.01 mol dm<sup>-3</sup> Zn(II) ions and 0.5 mol dm<sup>-3</sup> Na(I) ions. The results in this paper suggest that zinc electrodeposition from methanesulfonaic bath shows a similar electrochemical behaviour to that from a sulfate bath. Moreover, the ratio of anodic to cathodic charge was found to be consistent with the previous findings in sulfate bath. The charge ratio between the anodic and cathodic processes in methaneulfonate bath was 82% while the reported value in a sulfate bath was 81% [47]. This suggests that some of the charge during zinc electrodeposition was used for hydrogen evolution.

Plotting the logarithm of the current density vs. the potential range of zinc nucleation, a Tafel slope of  $-52 \pm 2 \text{ mV} \text{ decade}^{-1}$ was obtained which is almost the double the magnitude of the theoretical calculation of  $-30 \text{ mV} \text{ decade}^{-1}$  for a two electron transfer reaction. The value agrees with other works reported in the literature: Ibrahim [43] reported that the Tafel slope was



**Fig. 1.** Electrochemistry of zinc electrodeposition at a glassy carbon electrode in methanesulfonic acid. Electrolyte: 0.01 mol dm<sup>-3</sup> Zn(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> in 0.5 mol dm<sup>-3</sup> NaCH<sub>3</sub>SO<sub>3</sub> adjusted at pH 4 with CH<sub>3</sub>SO<sub>3</sub>H. (a) Cyclic voltammogram, from -0.80 to -1.40 V vs. Ag|AgCl at 20 mV s<sup>-1</sup> and 20 °C. (b) Randles-Sevcik plot, using potential sweep rates of 8, 16, 32, 64 and 128 mV s<sup>-1</sup>.

 $56 \text{ mV s}^{-1}$  at 0.09 mol dm<sup>-3</sup> zinc in 0.2 mol dm<sup>-3</sup> sodium sulfate. In the investigation of Guerra in zinc sulfate, the Tafel slope was *ca*.  $60 \text{ mV decade}^{-1}$  in neutral pH solution and *ca*.  $-30 \text{ mV decade}^{-1}$  in highly acidic electrolyte. The smaller Tafel slope (high cathodic current density) was due to the surface condition, as the hydrogen adsorbed on the newly formed zinc nuclei reacted. This resulted in the combined cathodic reactions of hydrogen evolution and zinc deposition, leading to a sharp increase in current density [48].

Fig. 1b shows a plot of the cathodic peak current densities *vs.* the square root of the potential sweep rate. For a mass transport controlled reaction, a linear increase of the peak current density with the square root of the potential sweep rate can be predicted by the Randles-Sevcik equation:

$$j_p = 2.69 \times 10^5 z^{1.5} D^{0.5} v^{0.5} c \tag{3}$$

where  $j_p$  is the peak current density, c is the zinc ion concentration in the electrolyte, z is the number of electrons involved the electrode process, v is the potential sweep rate and D is the diffusion coefficient of the zinc ions. From the Randles-Sevcik plot, the diffusion coefficient for zinc ions was found to be  $7.2 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>, while Meas et al. [49] reported a value of  $7.27 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> in hydrochloric acid. The value found here is comparable to previous estimations for the diffusion coefficient of zinc ions reported in the literature in other acid electrolytes: Yu et al. [31] calculated 2.1, 5.5 and  $8.4 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> in acetic, sulphuric and hydrochloric acids. The current used for zinc electrodeposition in methanesulfonic acid would be expected to be similar to that used in other common acids but the less-corrosive nature of methanesulfonic acid and its ability to dissolve high levels of metal ions makes it more attractive for energy storage applications.

#### 3.2. Linear sweep voltammetry

#### 3.2.1. Mass transport

As well as the charge-transfer process taking place on the electrode surface, mass transport of the Zn(II) ions towards the electrode contributes to the overall rate of the reaction. As the electrode potential becomes gradually more negative during the linear sweep voltammetry, the reduction of Zn(II) becomes dominated by the rate at which the ions reach the electrode surface. Fig. 2a shows a family of linear sweep voltammograms of Zn(II) reduction on a glassy carbon rotating disk electrode at various speeds: 400, 900, 1600, 2500 and 3600 rpm. The electrolyte composition was the same as that used in the experiments of Fig. 1a and b. In order to avoid excessive hydrogen evolution, the electrode potential was swept from -1.0 V to -2.0 V vs. Ag|AgCl at 20 mV s<sup>-1</sup>. The reduction of zinc was observed at the same potential as in the cyclic voltammogtam, -1.2 V vs. Ag|AgCl, and well defined plateau of constant current density where observed at potentials more negative than -1.4 V vs. Ag|AgCl. The constant supply of the zinc ions to the electrode surface due to the rotation of the electrode at different rates helps to maintain the Zn(II) ion concentration at the surface. An increased rotation speed was found to shorten the plateau region, leading to earlier hydrogen evolution.

The limiting current density for each rotating speed was measured at the mid-point of the plateau at -1.7 V vs. Ag|AgCl. The supply rate of zinc ions to the cathode surface is necessary to equalize with the rate of charge transfer. This is especially important during the charge and discharge of a redox flow battery; if the applied current density during the charge or discharge cycles is too high compared to the limiting current density, hydrogen evolution might take place instead of zinc electrodeposition or dissolution. The evolution of hydrogen can also increase the electrolyte resistance and reduce the effective plating area, which can result in burnt deposit [50]. Under such conditions, the transport rate of zinc ion to the surface of the negative electrode needs to be increased.

As shown in Fig. 2b, a linear relationship between the limiting current density with the square root of the rotation rate is observed and follows the Levich equation.

$$j_{\rm lim} = 0.620z F D^{2/3} \omega^{1/2} v^{1/6} c \tag{4}$$

where  $j_{\text{lim}}$  is the limiting current density (A cm<sup>-2</sup>), *F* is Faraday's constant,  $\omega$  is the rotation rate of the disk (rad s<sup>-1</sup>) and *v* is the kinematic viscosity of the electrolyte (cm<sup>2</sup> s<sup>-1</sup>). The linear behaviour indicates that the reduction of Zn(II) ions is under complete mass transport control. By using the gradient of Fig. 2b, a diffusion coefficient for zinc ions of  $7.8 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> was estimated. This value is slightly larger than the one obtained from the Randles-Sevik equation as possibly both hydrogen adsorption and oxygen reduction reactions are more significant under the mass transport controlled regime and contribute to a higher degree to the observed limiting current than in the cyclic voltammetry experiment. In this study, the average diffusion coefficient of zinc ion obtained from the Levich and Randles-Sevik equations in 0.01 mol dm<sup>-3</sup> zinc methanesulfonate and 0.5 mol dm<sup>-3</sup> sodium methanesulfonate at pH 4 is  $7.5 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>.

In the electroplating industry, high speed metal deposition is usually required and increasing the mass transport is a common strategy to provide a high current density and a fast electrodeposition rate. In the literature, it has been reported that powdery and burnt deposits can be avoided by increasing the limiting current density via enhanced mass transport techniques [35,50]. Turbulent flow and a high rate of cathode movement are often used for industrial high speed zinc electrodeposition [51].

#### 3.2.2. Zinc ion concentration

Fig. 2c shows the linear sweep voltammogram of zinc electrodeposition over a range of zinc concentrations of 10, 20, 40, 60 and  $80 \times 10^{-3}$  mol dm<sup>-3</sup> at 600 rpm rotation speed in 0.5 mol dm<sup>-3</sup> sodium methanesulfonate at pH 4 and 295 K. The electrode potential was swept from -1.0 to -2.0 V vs. Ag|AgCl at 20 mV s<sup>-1</sup>. As the concentration of zinc ions increased, the nucleation potential shifted towards positive values and changed linearly with the logarithm of Zn(II) ion concentration by  $58 \pm 2$  mV per 10-fold change in concentration. The magnitude of this potential shift is similar to that obtained in sulfate electrolytes reported in the literature [43].

Fig. 2d shows the limiting current densities for zinc deposition as a function of the concentration of the zinc ion. The limiting current density of zinc electrodeposition increased by *ca*.  $10 \text{ mA cm}^{-2}$  per every 10 mM zinc ion concentration. The linear plot confirms the fact that the system was under mass transport control according to the Levich equation. The potential window of the limiting current plateau decreases as the concentration of zinc increases suggesting that hydrogen evolution was more favourable as more zinc was deposited on the electrode surface.

#### 3.2.3. Concentration of protons

Fig. 3a shows the linear sweep voltammogram of zinc electrodeposition over a range of pH from 0 to 4 at the rotation speed of 600 rpm. The electrolyte composition is the same as in Fig. 1. The electrode potential was swept from -1.0 to -2.0 V vs. Ag|AgCl at 20 mV s<sup>-1</sup>. At higher pH values, the nucleation potentials were shifted towards more positive values, which is due to the higher conductivity of the electrolyte and to the increased concentrations of protons. Large limiting current plateaus were observed at pHs 4 and 3 than at lower pHs 0, 1 and 2.

At increased electrolyte acidity from pH 2 to 0, the stability of the zinc methanesulfonate complexes decreases and the reduction of protons occur on the newly formed zinc nuclei. This results in an undefined plateau at pH 0 and 1 and a slightly larger current density plateau at pH 2. At the lowest pH zinc electrodeposition competes with hydrogen evolution and the sharp increase in current density



**Fig. 2.** Effect of rotation speed and zinc ion concentration on zinc electrodeposition in methanesulfonic acid at glassy carbon electrode (293 K). (a) The effect of rotation speed on the cyclic voltammogram, (b) Levich plot, (c) the effect of zinc ion concentrations on the cyclic voltammogram and (d) the plot of zinc ion concentrations against the limiting current densities. Electrolyte: as in Fig. 1. Rotation speeds were 400, 900, 1600, 2500 and 3600 rpm. Zinc concentrations: 10, 20, 40, 60 and  $80 \times 10^{-3} \text{ mol dm}^{-3}$ . The electrode was swept from -1.0 to -2.0 V vs. Ag|AgCl scanning at 20 mV s<sup>-1</sup> at 600 rpm and 20 °C.



**Fig. 3.** Effect of electrolyte acidity and operating temperatures on zinc electrodeposition in methanesulfonic acid at glassy carbon electrode at 600 rpm. (a) Effect of electrolyte acidity on the cyclic voltammogram, (b) effect of electrolyte temperature on the cyclic voltammogram. Electrolyte: as in Figs. 1 and 2. Solution acidity was pH 4, 3, 2, 1 and 0. Electrolyte temperature: 20, 30, 40, 50 and 60 °C. The electrode was swept from -1.0 to -2.0 V vs. Ag/AgCl at 20 mV s<sup>-1</sup> and 20 °C.



**Fig. 4.** Effect of electrolytic additive on cyclic voltammogram of zinc electrodeposition in methanesulfonic acid (a) at static electrolyte and (b) at 600 rpm. Electrolyte: as in Figs. 1–3. Electrolytic additives were at 2 × 10<sup>-3</sup> mol dm<sup>-3</sup>, (i) no additive, (ii) potassium sodium tartarate, (iii) tetrabutylammonium hydroxide and (iv) indium oxide.

was due to the excessive hydrogen evolution. The competition of the deposition of zinc and hydrogen evolution has been confirmed by the reaction model reported by Cachet and Wiart [52], which stated that the discharge of zinc ion is firstly inhibited by hydrogen adsorption followed by the hydrogen evolution on the surface of the zinc deposit. At such highly acidic media, the zinc ion concentration on the electrode surface is relatively low and hydrogen adsorption on the electrode is hence easy. In this case, the current is mainly used for hydrogen evolution and the current efficiency of zinc deposition decreases.

The suppression of the hydrogen evolution reaction is necessary to promote zinc electrodeposition. In the system used by Plurion Inc., indium has been suggested as an additive to increase the hydrogen overpotential giving a current efficiency almost 95% compared to 70–80% without the additive [9,53]. Other finding suggests that additives, such as Na-benzylnicotinate [54], polyethylene glycol (PEG) [22,54], cetyltrimethyl ammonium bromide (CTAB) [32], tetrabutylammonium bromide (TEBACI)[55], perfluorosurfactants [56], tartaric acid [57], succinic acid [57], thallium [9], indium [12], cellulose [58] are capable of suppressing the hydrogen evolution reaction. In the plating industry, buffer reagents, for example H<sub>3</sub>BO<sub>3</sub>, are often incorporated to stabilize the pH and avoid excessive hydrogen evolution [59].

## 3.2.4. Operating temperature

Fig. 3b shows the linear sweep voltammograms of zinc electrodeposition over a range of electrolyte temperatures from 20 to 60 °C on a glassy carbon rotating disk electrode at 600 rpm. The electrolyte composition range is the same as that in the experiments described in Figs. 1 and 2. Both, the nucleation potential of zinc ions and hydrogen evolution potential shifted towards more positive values as the temperatures increased. The change in electrode potential obeys the Nernst equation, as a lower driving force for zinc electrodeposition and hydrogen evolution reactions is required as a higher temperature.

The electrode potential for the deposition of Zn(II) shifted 60 mV from -1.19 V vs. Ag|AgCl at 20 °C to -1.13 V vs. Ag|AgCl at 60 °C. Similar findings were observed by Zhang et al. [60] who reported that the cathodic potential decreased by *ca*. 65 mV when the temperature increased from 30 °C to 45 °C during zinc deposition in a sulfate electrolyte with 1-butyl-3-methylimidazolium hydrogen sulfate as an electrolytic additive. Elevated temperature can hence reduce the

polarization of zinc ions reduction effectively. Since diffusion coefficient is a function of temperature, the limiting current densities will increase; every 10 °C increase in the temperature of the electrolyte lead to an increase in current density of *ca*. 5 mA cm<sup>-2</sup>. During the zinc dissolution process (not shown) the charge of the zinc stripping peak was higher at elevated temperature confirming that zinc electrodeposition has been facilitated.

#### 3.3. Effect of electrolytic additives on the cyclic voltammetry

Electrolytic additives are often employed in the plating industry to obtain durable, uniform and more compact coatings as well as to decrease the rate of undesired reactions. Fig. 4a shows the cyclic voltammogram for zinc electrodeposition with the addition of three selected electrolytic additives: tetrabutylammonium hydroxide, potassium sodium tartarate and indium oxide at a glassy carbon static disk electrode. The concentration of the additives in all cases was  $2 \times 10^{-3}$  mol dm<sup>-3</sup> in an electrolyte containing 0.01 mol dm<sup>-3</sup> zinc methanesulfonate and 0.5 mol dm<sup>-3</sup> sodium methanesulfonate adjusted to pH 4 with methanesulfonic acid at 295 K. The potential was firstly swept from -0.8 V to -1.5 V vs. Ag|AgCl then reversed. The reduction and oxidation processes can be seen as the charge and discharge cycles of a half-cell zinc battery, respectively. Larger anodic peaks were observed with the addition of the additives except with tetrabutylammonium hydroxide. The ratio between the anodic and cathodic (discharge/charge) processes (Table 1) was 67%, whereas when indium oxide and potassium sodium tartarate were used, the ratio was approximately 88%. The addition of these two additives represented an improvement compared to the experiment in the absence of additives (82.3%). Despite the presence of indium oxide, single cathodic and anodic peaks were observed.

Linear sweep voltammograms in the presence of the three electrolytic additives were also carried out on a rotating vitreous carbon electrode disc at 600 rpm. Well-defined limiting current densities plateaus were observed in all the experiments but each additive presented different limiting current density value, this could be due to the additive reacting or adsorbing on the newly formed zinc deposit on the carbon electrode surface, thus decreasing the above surface area. Nucleation potentials of zinc in the presence of indium oxide and potassium sodium tartrate shifted to more positive values as shown in Table 1. This can be beneficial for battery

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Additive	Static electrode						Rotating electrode
	Nucleation	Cathodic peak		Anodic peak		Charge ratio (%) <sup>a</sup>	Limiting current density,
	vs. Ag AgCl (V)	Potential <i>vs.</i> Ag AgCl (V)	Current density (mAcm <sup>-2</sup> )	Potential vs . Ag AgCl (V)	Current density (mA cm <sup>-2</sup> )		Jim for zinc deposition at 600 rpm/mA cm <sup>-2</sup>
(i) No additive	-1.16	-1.19	-2.86	-1.03	5.8	82.3	-9.8
(ii) Potassium sodium tartarate	-1.15	-1.20	-2.60	-1.01	6.7	87.6	-8.3
(iii) Tetrabutylammonium hydroxide	-1.18	-1.22	-1.21	-1.05	4.2	66.6	-7.7
(iv) Indium oxide	-1.12	-1.18	-2.58	-1.01	7.5	87.7	-11.8

The electrochemical behaviour of the electrolytic additives: (i) no additives: (ii) potassium sodium tartarate, (iii) tetrabutylammonium hydroxide and (iv) indium oxide at static and rotating glassy carbon electrodes. The electrolyte

efficiencies, as lower charge voltages can be expected due to the reduced overpotential and zinc electrodeposition taking place prior to hydrogen evolution. The charge efficiency slightly improved except when tetrabutylammonium hydroxide was used. Although larger overpotentials obtained with tetrabutylammonium hydroxide result in lower voltage efficiency, such overpotentials were reported to be useful for refining the grain size and hence brightening the electrodeposit by partly covering the electrode surface and blocking the growth of the zinc crystals [61].

#### 3.4. Zinc half-cell efficiencies in a parallel plate flow cell

Aiming to achieve the optimum electrolyte compositions and operating conditions for a zinc-based redox flow battery, the electrodeposition and stripping of zinc were carried out over a wide range of concentrations, electrolyte flow rates, temperatures, applied current densities and electrolytic additives in a divided parallel flow cell. Unless indicated otherwise, the electrolyte composition was at  $1.5 \text{ mol dm}^{-3}$  zinc methanesulfonate in 1 mol dm<sup>-3</sup> methanesulfonic acid in the negative compartment while the other compartment contained 1 mol dm<sup>-3</sup> methanesulfonic acid. Electrodeposition of zinc on a carbon polyvinyl-ester composite substrate was carried out at 50 mA cm<sup>-2</sup> and 50 °C for 4 h. Table 2 summarizes the estimated half-cell efficiencies in terms of voltage, charge and energy at different operating conditions.

#### 3.4.1. Effect of operating parameters

Fig. 5a–c shows the effect of current density, temperature and electrolyte flow rate, respectively, on the charge–discharge curves of the zinc half cell reaction. In the absence of additives, the curves in Fig. 5a show that the largest energy efficiency was 70%, obtained at a low current density of 20 mA cm<sup>-2</sup> (Table 2). This high efficiency was attributed to the reduced ohmnic drop and improved voltage efficiency as the self-discharge of zinc became more significant while discharging at low current density. At a higher applied current density, the charge efficiencies were found to be higher but overall efficiency decreased. Similar findings were also reported by Saba and Elsherief [62] over a range of sulfuric acid and Zn(II) ion concentrations.

Fig. 5b shows the electrode potential vs. time at different temperatures during reduction and oxidation of zinc. Higher energy efficiency was obtained at lower operating temperatures, despite the fact that the solution conductivity and the resulting voltage efficiency increased with temperature. The charge efficiency significantly decreases from 94% at 20 °C to 68% at 70 °C. This is because higher temperature can lead to stronger depolarizing effect on hydrogen evolution than zinc deposition [63]; therefore less zinc was deposited at such a high temperature. Fig. 5c shows that as the mean linear electrolyte flow velocity increased from 1.8 to 5.8 cm s<sup>-1</sup>, an increase in charge efficiency was observed. This could be due to the fact that at a high mean linear flow velocity the diffusion layer broomes thinner and facilitates the transport of zinc ions to the working electrode. Despite this, larger voltage drop was also observed at a higher mean linear flow velocity. Therefore, the increase of electrolyte velocity did not significantly improve the overall energy efficiency of the zinc half-cell reaction.

#### 3.4.2. Effect of zinc ions and acid concentration

Electrolyte compositions, especially the concentration of acid, were found to be crucial for the flow cell performance. Energy efficiency was as high as 62% at 1 mol dm<sup>-3</sup> methanesulfonic acid compared to 41% at 3 mol dm<sup>-3</sup> methanesulfonic acid. Alfantazi and Dreisinger reported that electrical conductivity increase linearly with sulfuric acid concentration; therefore higher voltage efficiency was obtained [64]. Due to the more dominant hydrogen evolution reaction and faster corrosion rate at higher acid concentration, a

#### Table 2

Half-cell efficiencies of electrodeposition and stripping of Zn on a carbon polyvinyl-ester composite substrate from a methanesulfonic acid bath in a parallel plate flow cell. Unless indicated otherwise, the current density was 50 mA cm<sup>-2</sup>, deposition time 4 h, temperature 50 °C, mean linear flow velocity  $3.9 \text{ cm s}^{-1}$ . The solution was  $1.5 \text{ mol dm}^{-3} \text{ Zn}(CH_3SO_3)_2$  and  $1 \text{ mol dm}^{-3} \text{ CH}_3SO_3H$ .

Operating parameter	Zinc half cell overpotential $-\eta$ (V)	Zinc half-cell charge potential vs. Ag AgCl (V)	Zinc half-cell discharge potential vs. Ag AgCl (V)	Zinc half-cell efficiencies (%)		
				Voltage	Charge	Energy
Current density (mA cm <sup>-2</sup> )						
20	0.26	-1.17	-0.91	78	90	70
50	0.41	-1.28	-0.85	68	91	62
80	0.41	-1.30	-0.87	63	92	62
Temperature (°C)						
22	0.45	-1.32	-0.87	66	94	62
40	0.43	-1.31	-0.88	67	94	62
50	0.41	-1.28	-0.85	68	91	62
70	0.27	-1.19	-0.92	71	68	52
CH <sub>3</sub> SO <sub>3</sub> H concentration (mol dm <sup>-3</sup> )						
0.5	0.42	-1.26	-0.84	67	94	62
1	0.41	-1.28	-0.85	68	91	62
2	0.36	-1.24	-0.88	71	87	62
3	0.34	-1.24	-0.89	72	57	41
Zn <sup>2+</sup> concentration (mol dm <sup>-3</sup> )						
0.5	0.33	-1.27	-0.94	74	78	58
1	0.34	-1.24	-0.91	74	83	62
1.5	0.41	-1.28	-0.85	68	91	62
2	0.38	-1.21	-0.83	69	92	64
Mean linear flow velocity (cm s <sup>-1</sup> )						
1.8	0.33	-1.24	-0.92	74	86	63
3.9	0.41	-1.28	-0.85	68	91	62
5.8	0.37	-1.25	-0.88	70	92	64
7.8	0.41	-1.27	-0.86	67	92	62
Additive ( $\times 0.002 \text{ mol } dm^{-3}$ )						
No additive	0.41	-1.28	-0.85	68	91	62
Potassium sodium tartarate	0.35	-1.26	-0.91	72	86	62
Tetrabutylammonium hydroxide	0.44	-1.37	-0.93	68	39	26
Indium oxide	0.27	-1.21	-0.94	78	94	73

significant decrease in charge efficiency was observed. The increase in zinc ion concentration was found to facilitate the electrodeposition process indicated by the improvement of the charge efficiency but this does not improve the energy efficiency [64].

The lower charge cell voltages observed as the concentration of Zn(II) ions increases can be explained by the Nernst equation. Since the dissolution of zinc back to Zn(II) species becomes more difficult at higher Zn(II) ion concentration in the vicinity of the electrode surface, lower discharge voltages were obtained. Despite this, higher Zn(II) ion concentration can be advantageous for redox flow battery as it allows the battery to charge at high current densities without mass transport limitations. Such a high concentration ensures that enough Zn(II) ions exist at all state of charges. In addition, two moles of methanesulfonic acid are formed per mol of zinc methanesulfonate during the electrodeposition reaction as shown in Eq. (1) [65]. In order to minimize the hydrogen evolution and facilitate zinc electrodeposition, higher Zn(II) ion concentration is preferred in the negative electrolyte.

# 3.4.3. Effect of electrolytic additives in the parallel flat plate flow cell

Three electrolytic additives from different categories were tested at a concentration of  $2 \times 10^{-3}$  mol dm<sup>-3</sup>. Both indium oxide [66] and potassium sodium tartarate [67] are inorganic additives, while tetrabutylammonium hydroxide is a surface active agent. In order to determine whether they are suitable additives for battery performance, charge–discharge experiments were carried out in the presence of these additives. The electrode potential during the charge/discharge cycle is shown in Fig. 5d. With the addition of indium oxide, the energy efficiency improved significantly from 62% without additive to 73% (Table 2). In this case, higher charge and voltage efficiencies were obtained. The high charge efficiency

obtained could be attributed to the large hydrogen overpotential of indium as an additive also observed in the Plurion Inc.'s zinc-cerium system [12], hence larger current values can be used for zinc electrodeposition. As presented in the voltammetry study in Section 3.3, lower deposition overpotential was observed. Hence, an improved voltage efficiency was expected in this electrolysis study, which is consistent with the previous finding of Yang and Lin [66] in their alkaline zinc-air battery.

The other two additives did not have a significant improvement on the half-cell efficiencies probably due to their strong adsorption and inhibiting effect (levelling property). Ganne et al. reported that some electrolytic additives could slow down the charge transfer reactions, poisoning the active kink sites and increasing the deposition overpotential [37]. For instance, the charge and energy efficiencies in the presence of tetrabutylammonium hydroxide were only 39% and 26%, respectively (Table 2). As a result, only indium oxide was suitable to be used as an electrolytic additive in a zinc-based hybrid redox flow battery.

#### 3.5. Coating morphologies

Fig. 6a–d shows the microstructures of the zinc electrodeposits using different additives at  $2 \times 10^{-3} \text{ mol dm}^{-3}$ : (a) no additive, (b) potassium sodium tartarate, (c) tetrabutylammonium hydroxide and (d) indium oxide. In the absence of additive, hexagonal-like crystalline structure was aligned plate-by-plate parallel to the substrate (Fig. 6a). This morphology is typical of zinc deposition and has already been observed in the literature [64,68]. On the uppermost of such hexagonal plates, a relatively rough, irregular plate-like structure was observed because of the continued growth and the stacking of the hexagonal platelet on the top of one another during the prolonged deposition for 4 h.



**Fig. 5.** The effect of current density, temperature, mean linear electrolyte flow rate and electrolytic additives of zinc half cell on a carbon polyl-ester composite substrate from a methanesulfonic acid bath in a parallel plate flow cell. Unless indicated, the current density was 50 mA cm<sup>-2</sup>, deposition time 4 h, temperature 50 °C, mean linear flow velocity 3.9 cm s<sup>-1</sup> and the solution was 1.5 mol dm<sup>-3</sup> Zn(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> and 1 mol dm<sup>-3</sup> CH<sub>3</sub>SO<sub>3</sub>H.

The mechanisms of such stacking behaviour from nucleation to growth have been discussed by a proposed model of Lee et al. [69] with schematic diagrams and microscope images in the medium of zincate.

In general, the microstructure of the zinc deposit without additive is quite smooth indicated by a shiny appearance without any nodule or dendrite. This finding is consistent with previous investigations that methanesulfonic acid can reduce the dendritic growth [10,27], which has been a major problem in the zinc-halogen redox flow batteries, leading to short circuit and hence reduced life cycle [70–73]. In a zinc–bromine system, zinc dendrite was observed at current density as low as 15 mA cm<sup>-2</sup> [3]. Therefore, methanesulfonic acid is attractive for zinc-based redox flow battery, as it not only minimizes the dendritic growth but also maintain high charge efficiency (91%) as discussed in Section 3.4.

With the addition of potassium sodium tartrate, similar microstructure of the rough, irregular plate-like structure was observed as in the absence of additive (Fig. 6b). Comparing with the previous micrograph, the hexagonal platelets were more difficult to distinguish and were mostly covered by the irregular plate structures. This was due to the faster growth rate of the zinc platelets at the lower overpotential of potassium sodium tartarate as sug-

gested in the voltammetric study of this work. In the presence of tetrabutylammonium hydroxide (Fig. 6c), the microstructure was very different and was formed by nano size needle-shaped structures. Similar morphology has been reported by Gomes and da Silva Pereira [68] in the presence of cetyl trimethyl ammonium bromide in the sulfate medium. The needle-shaped microstructure was due to the competition between nucleation and crystal growth by the strong blocking effect of the absorbed surfactant as discussed in Section 3.5. The strong blocking effect and the adsorption of tetrabutylammonium hydroxide has been examined by the low charge and voltage efficiencies in the deposition and stripping experiment in a parallel flow cell (Section 3.4.3).

Among the additives tested, indium oxide had the highest half-cell efficiencies and a significant effect on the cell voltage. Due to the low deposition overpotential, zinc deposited at a faster rate and boulder-like agglomerates were observed after the addition of indium oxide. The boulder structure as shown in Fig. 6d has been considered to be a precursor of dendrites but the latter will not necessarily develop [74]. In this work, relatively rough and nodular morphology was observed instead of dendrites. On the coating surface, a small amount of indium (0.55 wt.%) has been detected by the energy-dispersive spectroscopy. In all



**Fig. 6.** The effect of electrolytic additives on microstructure of zinc electrodeposits obtained on a carbon polyvinyl-ester composite for a methanesulfonic acid bath in a beaker. Electrolytic additives  $2 \times 10^{-3}$  mol dm<sup>-3</sup>, (i) no additive, (ii) potassium sodium tartarate, (iii) tetrabutylammonium hydroxide and (iv) indium oxide. Electrolyte compositions and operating conditions were as in Fig. 5 but stirring at 400 rpm.

electrodeposits, no dendrite has been observed after depositing for 4 h at 50 mA cm<sup>-2</sup> in the absence or presence of the electrolytic additives.

#### 4. Conclusions

Zinc electrodeposition from 0.01 mol dm<sup>-3</sup> Zn(II) ions in methanesulfonic acid is a mass transport controlled process and with a zinc ion diffusion coefficient of  $7.5 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> obtained from the Randles-Sevick and Levich equations.

At a higher acid concentration, a significant decrease in charge efficiency was observed due to more dominant hydrogen evolution and faster corrosion rate. Although higher zinc ion concentration led to more difficult dissolution process, it is still advantageous for redox flow battery application as not only facilitates the deposition process, but also allows the battery to charge at a high current density without mass transport limitation and ensures enough Zn(II) ions at all state of charge. The optimum electrolyte compositions for flow battery application were suggested at high zinc(II) methanesulfonate concentration  $(1.5-2 \text{ mol dm}^{-3})$  and at low methanesulfonic acid concentration (i.e. 0.5 mol dm<sup>-3</sup>).

In the presence and absence of the electrolytic additives tested, no dendrite was observed in all zinc electrodeposits at 50 mA cm<sup>-2</sup> and 60 °C over 4 h. The low deposition overpotential observed with the addition of  $2 \times 10^{-3}$  mol dm<sup>-3</sup> potassium sodium tartarate and indium oxide led to irregular, layer-like and granular microstructures, respectively. Among the three additives tested, only indium oxide was suitable for zinc-based redox flow battery as energy efficiency improved significantly from 62% in the absence of additives to 73% due to the improvement of both charge and voltage efficiencies in the presence of additives.

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