Effects of Electrolyte Concentration, Temperature, Flow Velocity and Current Density on Zn Deposit Morphology

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Abstract: The most critical disadvantages of the Zn-air flow battery system are corrosion of the zinc, which appears as a high self-discharge current density and a short cycle life due to the non-uniform, dendritic, zinc electrodeposition that can lead to internal short-circuit. In our efforts to find a dendrite-free Zn electrodeposition which can be utilized in the Zn-air flow battery, the surface morphology of the electrolytic Zn deposits on a polished polymer carbon composite anode in alkaline, additive-free solutions was studied. Experiments were carried out with 0.1 M, 0.2 M and 0.5 M zincate concentrations in 8 M KOH. The effects of different working conditions such as: elevated temperatures, different current densities and different flow velocities, on current efficiency and dendrite formation were investigated. Specially designed test flow-cell with a central transparent window was employed. The highest Coulombic efficiencies of 80%-93% were found for 0.5 M ZnO in 8 M KOH, at increased temperatures (50-70 °C), current densities of up to 100 mA·cm⁻² and linear electrolyte flow velocities higher than 6.7 cm·s⁻¹.

Key words: Dendrite, electrochemistry, flow battery, zinc, zinc morphology.

1. Introduction

With the rapidly increasing demand for efficient use of renewable, clean, but often intermittent and difficult to predict sources of energy, such as solar power and wind, it is necessary to develop sustainable and low cost energy storage systems. Redox flow batteries with their ability to store relatively cheaply large amounts of electrical energy, promise to meet these requirements. The very first flow battery was constructed by Charles Renard in 1884. Renard used zinc and chlorine as the reactive elements to power his army airship La France. Further developments were made many years after, by NASA (National Aeronautics and Space

Administration) scientist Thaller in 1974. Thaller's redox flow battery was comprised of iron and chromium [1]. Since that time, the design of the redox flow battery systems has evolved as witnessed by review of the numerous papers that have been published over the last four decades [2-15]. And yet, this field is still in its infancy due to the lack of suitable electrode and electrolyte materials, together with difficulties in mastering the interfaces between them. Most redox flow battery systems require expensive ion-exchange membranes to separate the two electrolytes. However, the so-called single electrolyte flow battery systems avoid the need for a membrane. One of the most promising candidates in this field is the rechargeable Zn-air flow battery [16]. Zinc is an attractive material for secondary alkaline batteries due to the high energy density, low equilibrium potential, high hydrogen overpotential, low cost, high abundance

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and environmental friendliness [17, 18]. Upon charging, zincate ions are electrochemically reduced to metallic zinc. Zn deposits can grow with different morphologies, described as: filamentous mossy, spongy and dendritic [19]. The most critical disadvantages of the Zn-air flow battery system are corrosion of the zinc, which appears as a high self-discharge current density, and a short cycle life due to the non-uniform, dendritic, zinc electrode position that can lead to internal short-circuit [20-22]. Another problem to address is the hydrogen evolution, which significantly affects the morphology of deposits. In turn, the deposit morphology has an influence on the Coulombic efficiency of the charge/discharge cycle. At the beginning of charging, depending on the type of electrode used, the active surface area for zinc deposition can be small, thus the release of hydrogen bubbles can cause dendrite formation and potential oscillations in the cell [23]. Many attempts have been made in order to improve the appearance and physico-chemical properties of the deposits by introducing various organic and inorganic additives [24-27]. However, the effect of electrolyte concentration on the current efficiency of the alkaline zinc processes together with temperature and especially electrolyte flow velocity on the resultant morphological properties, to the best of our knowledge have not been reported quantitatively in the literature [28-31]. Therefore, this work is focused on the morphology of zinc electrodeposited from different additive-free alkaline zincate solutions which can be utilized in the rechargeable zinc-air flow batteries. The effects of different working conditions, such as elevated temperatures, different current densities and different electrolyte flow rates, on current efficiency and dendrite formation, for specific bath compositions are reported.

2. Experimental Section

Prior to the flow cell experiments, Rota-Hull cell (Eco Chemie B.V., Utrecht, Holland) experiments in various KOH, additive-free, zincate solutions on brass

cylinder electrodes with a diameter of 6 mm and an active surface area of 15 cm², have been carried out. The Rota-Hull cell experiments were performed in order to accelerate screening and to identify the most promising parameter combinations which could be further tested in the flow cell. The counter electrode was a platinized titanium mesh. The electrolyte volume was 700 mL. Zinc was deposited at 25, 30, 50 and 70 °C, rotation rates of 95, 191 and 509 rpm, which corresponds to the linear flow velocities: 3, 6 and 16 cm·s⁻¹, respectively and ZnO concentrations of 0.1, 0.2 and 0.5 M. In cases where two different Zn deposit morphologies were observed, there was an intermediate zone of mixed morphology. From a known correlation between primary current density and position on the electrode, the first occurrence of dendrites in an otherwise mossy deposit was used to determine the transition current density.

For the investigation of Zn plating and stripping in flowing electrolyte, a special test rig was constructed. The test rig was equipped with: two flow-meters for different flow ranges (Bio-Tech 97478625 and Bio-Tech 97478321, Germany), two differential pressure sensors (Motorola- Freescale MPX-2010 DP, United Kingdom), an electrolyte heater made from stainless steel (Galvatek ROTKAPPE FC 27, Finland), a PT100 temperature sensor (Galvatek SOPT2 F2000T0, Finland) and an AC magnetically- coupled centrifugal pump (Sondermann RM-PP-EKKK-2/20-30(30)-60-3-G, Germany). An IM6 Potentiostat-Galvanostat (ZAHNER-elektrik GmbH, Germany) was used as the power source for the electrochemical test flow half-cell. The test flow cell, for studying the Zn- half cell of the Zn-air flow battery, was designed by C-Tech Innovation Ltd (Fig. 1). The test flow cell was connected with a 5 L tank of electrolyte. The electrolytes used for the experiments were concentrated aqueous KOH solutions (Sigma Aldrich, 99.99%) containing dissolved ZnO (Sigma Aldrich, 99.99%). All electrolytes contained 8 M KOH. The KOH electrolyte was chosen in preference to

NaOH due to its high conductivity and faster kinetics for the zinc deposition as well as the oxygen reduction process. The solubility of ZnO in different KOH concentrations and the viscosity of these solutions have been previously determined [21]. It was found that, for KOH concentrations higher than 8 M, the viscosity increases sharply. It was also found that, the oxygen solubility decreases with higher alkaline content, which is detrimental to the performance of the air electrode [21]. Based on these findings, the concentrations of dissolved ZnO were chosen to be: 0.1 M, 0.2 M and 0.5 M for three different electrolytes. No additives were used. During the flow cell experiments, metallic zinc was deposited on a polished polymer carbon composite, ElectroPhen® (BAC2 Limited, Romsey, United Kingdom) with 10 cm² geometric surface area, serving as current collector. The second electrode, aligned parallel to the first and of similar area, was a Zn plate (Advent Research Materials Ltd, United Kingdom, purity 99.5%). The initial gap between both electrodes was 5 mm. During cycling, it was possible to visually inspect the morphology of the Zn deposits, as well as the evolution of hydrogen and oxygen at the electrodes through a central transparent window of the test flow cell (Fig. 1). Scanning electron microscopy (SEM, XL30 Field Emission ESEM, with High-Brightness Field Emission Gun-FEG, Field Electron and Ion Co., Nederland) was used to study the morphology of the Zn electrode after disassembling the cell and subsequent rinsing with deionized water and drying.

Flow cell experiments were carried out at 25, 30, 50 and 70 °C, in combination with current densities of 10, 50 and 100 mA·cm⁻² as well as electrolyte flow rates of 0.2, 0.5 and 0.8 L·min⁻¹. The latter correspond to linear flow velocities of 6.7 cm·s⁻¹, 16.7 cm·s⁻¹ and 26.7 cm·s⁻¹, respectively (calculated for the interelectrode gap prior to deposition). Each cycling experiment consisted of 24 cycles. Each cycle consisted of 30 min plating followed by stripping until the cell potential difference reached 600 mV. The next plating step commenced

Fig. 1 Two-electrode, electrochemical test flow half-cell. The transparent window in the middle of the test flow cell (magnified as an example in the right corner- circles, with: (a) electrodeposited compact and dendrite-free Zn layer and (b) electrodeposited dendritic Zn layer on BAC2 electrode), provides opportunity for an in-situ visual study of the surface morphology of the Zn deposits. In-situ monitoring and control of the electrolyte flow speed, pressure difference and electrolyte temperature is possible.

immediately following the stripping step. Cyclic voltammograms were recorded using (VoltaLab PGZ301 Radiometer Analytical), on a BAC2 electrode, in the voltage range -0.1 V to -2.5 V vs. Hg/HgO of additive free 0.1 M, 0.2 M and 0.5 M ZnO in 8 M KOH at room temperature and at 50 °C, respectively. The sweep rate was 50 mV·s⁻¹ and a Pt plate with 10 cm² geometric surface area was used as counter electrode.

For investigation of the grey residue, found at the bottom of the electrolyte tank, an X-Pert powder diffractometer (PAN-alytical, Netherlands) with Cu-K α radiation in Bragg-Brentano geometry, at 40 kV and 30 mA was used.

3. Results and Discussion

3.1 Cyclic Voltammetry

In each curve in Fig. 2a, there is a well-defined reduction peak for zincate, at -1.69 V (0.1 M), -1.70 V (0.2 M) and -1.85 V (0.5 M) in the cathodic scan and an

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Fig. 2 Cyclic voltammograms in stagnant 0.1 M, 0.2 M and 0.5 M potassium zincate solutions at BAC2 electrode at: (a) room temperature and (b) 50 °C. Between experiments, electrolytes were purged with air. The initial sweep was in cathodic direction with a starting potential of ca. -1 V vs. Hg/HgO. The sweep rate was 50 mV·s⁻¹ and Hg/HgO was used as reference electrode.

oxidation peak at -1.27 V (0.1 M), -1.10 V (0.2 M) and at -0.90 V (0.5 M) in the anodic scan, indicating dissolution of the bulk zinc layer. A shoulder in the peak for Zn stripping is observed in Fig. 2b. Such shoulders or double peaks in anodic stripping presumably appear due to the fact that the zincate solubility limit was temporarily exceeded in the diffusion layer. Somewhat higher current densities for reduction and oxidation peaks in Fig. 2b, in comparison to the corresponding cyclic voltammograms in Fig. 2a, indicate higher diffusion rates at 50 °C due to the decrease in electrolyte viscosity and therefore higher migration.

3.2 Rota-Hull Cell Experiments

The Rota-Hull cell study is used for the pre-screening of Zn deposit morphology over a wide range of current densities, for different hydrodynamic conditions. Zinc was deposited for 30 min and a mean current density of 50 mA·cm⁻². The Rota-Hull cell zinc deposits from 8 M KOH containing 0.5 M ZnO showed a transition from the filamentous mossy zinc morphology at lower current densities to the dendritic zinc morphology at the higher current densities. The current density of the transition zone shifted to higher current densities with increasing linear flow velocities, Fig. 3.

As an example, the SEM micrograph of the dendritic Zn deposit obtained at room temperature, at 50 mA·cm⁻² current density and with 3 cm·s⁻¹ linear flow velocity is shown in Fig. 4. Higher operating temperatures in the rechargeable zinc-air flow battery should increase the electrolyte conductivity and salt solubility and also the kinetics of the air electrode. Therefore, it was of particular interest to examine the effect of electrolyte temperature on the Zn plating and dissolution under these conditions. By increasing the electrolyte temperature to 70 °C, at all rotation rates/linear flow velocities and current densities of $j \leq 50$ mA·cm⁻², dark-grey mossy zinc deposits were obtained. These

Fig. 3 Morphology pattern of the zinc deposits from Rota-Hull cell experiments at different electrolyte temperatures and various electrolyte flow velocities, in additive-free 8 M KOH containing 0.5 M ZnO. The deposition time was 30 min and a mean current density of 50 mA·cm⁻² was applied.

Fig. 4 SEM micrograph of the dendritic Zn deposit obtained from 0.5 M ZnO in 8 M KOH at room temperature, with a linear flow velocity of $3 \text{ cm}\cdot\text{s}^{-1}$ and a current density of $50 \text{ mA}\cdot\text{cm}^{-2}$ on a brass cylinder electrode.

deposits showed a moderate mechanical stability against water rinsing (wash bottle).

The dark-grey colored filamentous mossy deposits obtained from 0.5 M zincate in 8 M KOH at 70°C , current density of $50 \text{ mA}\cdot\text{cm}^{-2}$ and linear flow velocity of $6 \text{ cm}\cdot\text{s}^{-1}$ are shown in Fig. 5. At constant temperature and increasing flow velocity of the electrolyte, the transition from the filamentous mossy to the dendritic zinc morphology was shifted to higher current densities.

This can be explained by the increased convection, shifting the limiting current density to higher values. It was also found that, at a constant linear flow velocity and increasing electrolyte temperature, the transition point from filamentous mossy to dendritic zinc morphology was shifted to higher current densities. With increasing temperature, the electrolyte viscosity is decreased, hence the ionic mobility of the zincate ions is increased. The increased mobility of the zincate ions shifts the limiting current density to the higher values. During extended periods of charging and discharging of the secondary zinc-air flow battery, the zincate concentration in the electrolyte varies significantly. Thus, it is important to know for which combinations of parameters (temperature, current density, flow rate) at a given zincate concentration dendrites start to grow.

Based on the results of Rota-Hull cell experiments, electrolytes with 0.1 M ZnO gave dendritic deposit

(a)

(b)

Fig. 5 (a) SEM micrograph of the filamentous mossy zinc deposits from 0.5 M zincate in 8 M KOH at 70°C , at a current density of $50 \text{ mA}\cdot\text{cm}^{-2}$ and a linear flow velocity of $6 \text{ cm}\cdot\text{s}^{-1}$. (b) Same as for micrograph (a) but at higher magnification.

morphologies at all temperatures, rotation rates and current densities. A small window for spongy deposit morphology was observed only at 70°C , a flow velocity of $16 \text{ cm}\cdot\text{s}^{-1}$ and current densities lower than $13 \text{ mA}\cdot\text{cm}^{-2}$.

It is well known that growth of different deposit morphologies is a rather complex process. Various kinetic and thermodynamic properties play a role in electrocrystallization [31, 32]. When zincate is reduced, the hydroxide ion concentration increases at the electrode and affects the reaction. This change in the kinetic and thermodynamic conditions of the zincate reduction reaction results in the initiation of a mossy morphology (Figs. 5a and 5b). Hence, the deposition conditions favoring mossy zinc are higher zincate concentrations, higher temperature and a surface which

provides a high number of nucleation centers. The formation of the mossy morphology is under activation control in contrast to diffusion controlled dendritic growth.

3.3 The Flow Cell Experiments

After the Rota-Hull investigations, flow cell experiments were performed. In each experiment, a 1 h long deposition/dissolution cycle was repeated twenty-four times. As an example, several voltage vs. time figures (Zn plating/stripping under galvanostatic control) for 0.5 M zincate concentrations in 8 M KOH at various temperatures are shown in Fig. 6. During plating/stripping cycles, a ZAHNER-elektrik Potentiostat's software was programed to limit the maximum stripping voltage to 600 mV, thereby protecting the carbon electrode from corrosion. Thus when the stripping potential reached the 600 mV, a new plating was immediately unleashed regardless the initially planned length of the stripping cycle. Reader should note that, these results corresponding solely to the measurements of the Zn-half of the Zn-air flow battery, where in the two-electrode, electrochemical test flow system metallic zinc was deposited on a polished polymer carbon composite and in the same time zinc was dissolved at the second electrode (Zn plate), aligned parallel to the first one (Fig. 1). It was found that, at 0.5 M ZnO concentration, the Coulombic efficiency for each set of parameters at room temperature ranges from 64% to 80%.

Dendrite formation is observed only at the highest current density of $100 \text{ mA}\cdot\text{cm}^{-2}$ in combination with the lowest flow rate of $6.7 \text{ cm}\cdot\text{s}^{-1}$. Such a discrepancy between the results obtained with the Rota-Hull cell (Fig. 3) and with the flow cell (Fig. 7) cannot be simply explained by the theories of mass transfer in various cell geometries. Although the linear flow velocities are in the same range, the transition from laminar to turbulent flow occurs at much lower Reynolds numbers in the Rota-Hull [33] compared to the flow cell experiments [34]. Thus, the different substrate

materials in both set-ups as well as the different conditions for the release of hydrogen bubbles from the surfaces due to different electrode geometries are more likely to play decisive role here for the morphology of the Zn layers.

The electrodeposition in highly alkaline electrolytes produces predominant mossy or spongy zinc deposits. The spongy type deposits (Fig. 8) are mainly formed at higher temperature ($T = 70 \text{ }^{\circ}\text{C}$) and high current density ($j = 100 \text{ mA}\cdot\text{cm}^{-2}$). The adherence of the mossy zinc layers is found to be better than that of the spongy type zinc deposits.

The fact that spongy deposits are observed only at higher temperatures is important, because detachment of zinc particles can occur when the sponge type zinc dissolves on discharging. These zinc particles are sparingly soluble in the electrolyte, due to their low corrosion rate in KOH. This is experimentally confirmed. Namely, the detached particles are found at the bottom of the electrolyte tank in the form of a grey residue. The residue was collected, rinsed in deionized water, dried and examined by X-ray diffraction. This qualitative analysis confirmed that the grey powder exclusively consisted of Zn and ZnO crystalline phases.

By decreasing the zincate concentration in the electrolyte, the Coulombic efficiency decreased to 49%-78%. This decrease of Coulombic efficiency is more pronounced at higher temperatures, which is probably caused by increased reaction rates of hydrogen evolution and of zinc corrosion. The onset of dendrite formation also increased for decreasing zincate concentration. For example, dendrites were observed at $50 \text{ }^{\circ}\text{C}$, $50 \text{ mA}\cdot\text{cm}^{-2}$ and maximal flow rates of $26.6 \text{ cm}\cdot\text{s}^{-1}$ at 0.1 M ZnO, while the same conditions with 0.2 M ZnO gave dendrite-free deposits.

The key findings (limiting conditions for onset of dendrite growth) extracted from this work and corresponding to the flow cell experiments are summarized in Figs. 7 and 9.

Fig. 6 $c = 0.5 \text{ M ZnO}, j = 50 \text{ mA}\cdot\text{cm}^{-2}, v = 16.7 \text{ cm}\cdot\text{s}^{-1}$. (a) $T = 25 \text{ }^{\circ}\text{C}$, (b) $T = 50 \text{ }^{\circ}\text{C}$ and (c) $T = 70 \text{ }^{\circ}\text{C}$. At the end of each stripping cycle, the voltage rises when there is no more Zn to strip.

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Fig. 7 Morphology of the zinc deposits in flow cell experiments as function of current density at two different electrolyte temperatures and three electrolyte flow velocities, from additive-free 8 M KOH containing 0.5 M ZnO.

Fig. 8 (a) SEM micrograph of the spongy zinc deposits from 0.5 M zincate in 8 M KOH at 70 °C, current density of 100 mA·cm⁻² and linear flow rate of 6.7 cm·s⁻¹. (b) Same as for micrograph (a) but at higher magnification.

Fig. 9 Morphology of the zinc deposits in flow cell experiments as function of current density at two different electrolyte temperatures and three electrolyte flow velocities, from additive-free 8 M KOH containing 0.1 M ZnO.

According to Figs. 7 and 9, recommendation for Zn(II) in a Zn-air flow battery using KOH electrolytes without additives could be found between the concentration limits of 0.5 M to 0.2 M, for any set of parameters (current density, linear flow velocity, temperature) used within this work.

Therefore, the usable charge density of an additive-free Zn-air flow battery electrolyte may be derived from the most advantageous Zn(II) concentration range of 0.2-0.5 M, which corresponds to 16 Ah·L⁻¹ for the later one. Although this is rather low compared to some secondary portable batteries it is within the range of other proposed stationary energy storage technologies [35].

4. Conclusions

It was found that, dendrite-free Zn electrodeposition from additive-free alkaline zincate solutions is possible in a practical concentration range. The electrodeposition in highly alkaline electrolytes produces predominant mossy or spongy zinc deposits. Spongy deposits showed poor adherence to the carbon substrate. Once detached, these deposits are sparingly soluble in the electrolyte. The deposition conditions favoring mossy zinc are higher zincate concentration,

higher temperature and a surface which provides a high number of nucleation centers. Raising the current density promotes the formation of dendritic deposits. The highest Coulombic efficiencies of 80%-93% were found for 0.5 M ZnO in 8 M KOH, at elevated temperatures of 50-70 °C, current densities of up to 100 mA·cm⁻² and linear electrolyte flow velocities higher than 6.7 cm·s⁻¹. Although the electrolytes with 0.2 M ZnO gave filamentous mossy zinc deposits at all combinations of parameters, it was found that, zincate concentrations lower than 0.5 M result in a decrease of Coulombic efficiency and further shedding can lead to a continuous fading of available capacity in the flow battery.

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