



The influence of a chloride-based supporting electrolyte on electrodeposited zinc in zinc/bromine flow batteries

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ARTICLE INFO

Article history:

Received 21 June 2018

Received in revised form

22 August 2018

Accepted 28 August 2018

Available online 21 September 2018

Keywords:

DFT

Secondary electrolyte

Zinc bromine flow batteries

Zinc chloride

Zinc electrodeposition

ABSTRACT

A combination of analytical techniques and molecular modelling methods was used to study the influence of chloride-based supporting electrolytes on zinc electrodeposit surfaces in the zinc half-cell of zinc/bromine flow batteries. Scanning electron microscopy and X-ray diffraction analysis of zinc electrodeposits obtained during charging show that: (a) the primary preferred orientation is planar, and (b) increasing the duration of exposure to the Cl-containing electrolyte influences crystallinity and changes the preferred secondary orientations. Analysis using periodic density functional methods indicates that the binding energy of Cl to the Zn(001) surface depends more strongly on surface coverage than on binding site location. Solvation increases the stability of Cl binding to the surface. The binding energies of Cl with and without water solvation are between 288 and 327 kJ mol⁻¹ and 249–288 kJ mol⁻¹, respectively, for coverages between 0.11 and 0.33 ML. The binding of Cl leads to Zn surface buckling and decreases surface uniformity. Binding at 0.33 ML and above results in surface instabilities, leading to the formation of surface cavities due to significant vertical displacement of surface Zn sites.

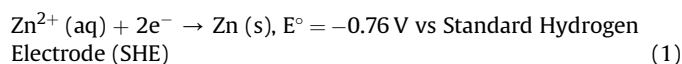
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1. Introduction

Renewable power sources such as solar and wind are variable in nature. Hence their use in a reliable power system can be troublesome without adequate dispatchable power sources. Besides avoiding such flux issues, the pursuit of highly efficient storage technology would also facilitate the integration of renewables into existing grid networks [1–4]. Flow battery technology can offer a practical solution to this problem. The zinc/bromine battery (Zn/Br RFB) [5] is a particularly attractive option due to its low cost of electrolyte materials [6] and high theoretical specific energy of 440 Wh kg⁻¹ [7,8]. The main electrolyte in Zn/Br RFBs is zinc bromide (ZnBr₂) which functions as the primary participant in charge-transfer reactions at the electrodes. High concentrations of ZnBr₂ between 1 and 3 M are commonly used [9], while electrolyte pH is usually maintained between 1 and 3.5 to avoid zinc deposits with dendritic and mossy appearance [10,11] which are usually indicative of poor battery performance. Results from separate ongoing

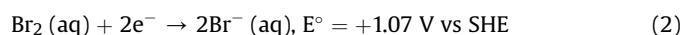
and previous work in this area show that pH changes can be seen with varying chloride concentrations due to changing lability of protons in solution, with implications for double-layer capacitance (due to tightness of ion packing as well as the sizes and proportions of ions themselves) and charge transfer impedances at the electrode/zinc surface [12,13].

The following reaction (Eq. (1)) takes place in the zinc half-cell when the battery is being charged and is essentially similar to that of zinc electroplating [7,14].



Zinc dissolves back into the aqueous electrolyte upon discharge of the battery, thereby releasing electrons via the bipolar electrode stack.

The following reaction (Eq. (2)) occurs on the bromine side during discharge [15,16].



A quaternary bromide salt such as N-methyl N-ethyl pyrrolidinium bromide (MEP) [17] is added to sequester elemental bromine as it is formed and trap it in a separate oily phase until the battery is

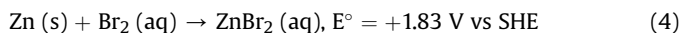
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ready to be discharged. The sequestering agent is usually added in an approximately 1:3 M ratio to ZnBr_2 [9,18]. Combining the individual half-cell processes gives the overall redox reaction for the system, whereby the primary ZnBr_2 electrolyte produces zinc electrodeposits and evolves elemental bromine during charging, as shown in Eq. (3):



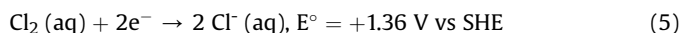
The converse occurs during battery discharge, whereby zinc and bromine recombine to form aqueous zinc bromide, as shown in Eq. (4):



The theoretical electrochemical potential of a single cell based on individual half-cell potentials should be approximately 1.83 V. However, internal resistances cause cell voltages to be slightly lower in practice.

The present work focusses on understanding the interactions between solutes with electrodeposited zinc in the zinc half-cell in a Zn/Br RFB. The degree of zinc deposit compactness has a direct influence on battery performance [19] and current efficiencies are linked to the morphology of electrodeposits [20]. Compactness of zinc deposits is related to improvements in plating density and higher surface coverage which results in lesser zinc remaining on the electrode after practical discharge is complete. Even during the later stages of discharge, there will be a higher local current density required if an overall galvanostatic discharge is to be maintained. Uniform zinc plating is necessary to achieve good current densities as it effectively utilizes the available electrode surface area. Conversely, poor deposition with dendritic features or kink sites reduces current densities even for high-conductivity electrodes. Dendrites also risk puncturing the separating membrane in full-cell systems. In order to make beneficial changes to the Zn/Br system, it is first necessary to understand the fundamental reactions occurring between species already existing in conventional electrolyte solutions. Specifically, it is important to identify which components might potentially be influencing zinc deposition negatively and use this information to seek suitable alternatives in order to improve battery performance.

Chloride-based additives such as potassium chloride, sodium chloride, and ammonium-based chlorides [7,21,22] can be included as supporting electrolytes to maintain ionic conductivity of the solution when the primary electrolyte ions are depleted during charging. Building upon previous work in this area where Br influences are electrochemically studied and found to strongly influence zinc electrodeposition [23], the present work focusses on the effects of Cl. The reduction of chlorine (Eq. (5)) occurs as follows [14].



Chlorides are presently considered suitable for use as secondary electrolytes as chlorine has a higher reduction potential than bromine (difference of 0.29 V vs SHE) and is not expected to interfere with the bromine-side redox process during battery operation. However, there exists a possibility that the use of chlorides could have negative effects on zinc half-cell performance, given that zinc is susceptible to corrosion by chloride-containing species [24] and aqueous chlorine is effective at leaching solid zinc [25]. It has long been known that zinc chloride concentration has a major influence on the surface roughness of zinc deposits obtained from such solutions [26], and it has been reported that zinc electrodeposited from zinc chloride solutions produced rough

deposits which were also porous [20]. Chlorides have been found to influence the characteristics of zinc deposits above concentrations of 500 mg L^{-1} [27], which is of relevance to the present work as conventional Zn/Br secondary electrolytes can have significantly higher chloride concentrations of about $34,000 \text{ mg L}^{-1}$ (i.e. 2 M). There has also been recent work to replace chloride-based additives with other anions [23], including perchlorates [28], with positive results.

The use of ethylene diamine and ammonia additives to inhibit chloride adsorption onto the electrode surface has shown that controlling the electrical double-layer is a key factor influencing zinc deposit structure [29]. This inhibition occurs by altering the nucleation mechanism and growth rate, influencing the homogeneity of crystal size distribution. Electrochemical impedance spectroscopy (EIS) investigations of zinc deposition from chloride-based electrolytes have also indicated that chlorides could potentially be adsorbed onto the zinc surface [30]. Nucleation overpotential for the deposition of zinc from 3 M ZnCl_2 electrolytes is slightly higher than for ZnBr_2 electrolytes of similar concentration [31], indicating that chlorides reduce the zinc deposition and stripping efficiency. Zinc bromide complexes also have lower stability constants but faster kinetics compared to those of zinc chloride. Comparison of zinc deposits from pure chloride-based electrolytes against those with citrate additive in zinc/polyaniline batteries has shown the latter to produce smoother deposits whereas the former promotes dendritic growth [32], indicating inhibition of negative effects caused by chlorides. The reason stated in literature for obtaining the smoother deposits was that citrate decreases exchange current density and increases the Tafel slope, lowering dendrite formation and the rate at which zinc corrodes.

The experimental observations described above may be explained *via* molecular modelling of the interactions between Cl and zinc surfaces. Previous literature involving Density functional theory (DFT) calculations and Zn(001) is limited to Zn adatom migration across that surface [33]. To the best of our knowledge, however, studies on interactions between Cl/ Cl_2 and the Zn(001) surface have not been reported. Furthermore, most DFT studies related to energy storage have been carried out for lithium-based systems whereas few exist for zinc-based batteries, such as the zinc/air battery [34]. The characteristics of the interaction between Cl and Zn surfaces such as surface restructuring, binding energies, and Cl surface diffusion paths have not been determined.

DFT has been used to study the interactions of Cl with different metallic surfaces as well as those exhibiting metallic behavior. Cl is reported to migrate rapidly across graphene surfaces with negligible energy barrier if it is bound to graphene with a significant binding energy, and chlorination of graphene at high coverage results in a buckled surface [35]. DFT and experimental investigations involving Au(111) found that Cl coverages above 0.33 monolayer result in surface saturation and system instabilities as Au atoms are removed from the surface to form an Au–Cl compound (a complex superlattice), ostensibly resulting in a more energetically stable configuration, and that Cl preferentially binds above fcc sites [36,37]. A similar saturation behavior is reported for Cl above Cu(111) [38]. DFT investigations of halogen–metal interactions with the (111) surface of metals such as Pd, Pt, Cu and Au, found that halogen–metal binding energies varies inversely with the size of the halogen atoms [39]. Cl binds to metals altering the morphology of the surface [36,37] and creates surface vacancies at high coverage [40].

The present work combines analytical techniques with periodic DFT approaches to study the influence of chloride-based supporting electrolyte concentration on zinc electrodeposited surfaces in the zinc half-cell of Zn/Br flow batteries. We first report experimental evidence of the effect that chlorides have on zinc electrodeposits

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