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Full Paper

Zinc Electrodeposition in the Presence of an Aqueous Electrolyte Containing 1-Ethylpyridinium Bromide: Unexpected Oddities*

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The reversible electrodeposition of zinc was investigated in an aqueous electrolyte containing zinc bromide (50 mM) and 1-ethylpyridinium bromide ($[C_2Py]Br$, 50 mM) by cyclic voltammetry, chronoamperometry, and scanning electron microscopy. Unusual voltammetric behaviour for the Zn/Zn^{II} redox couple was observed in the presence of $[C_2Py]Br$. Passivation of the redox couple was observed after a single deposition–stripping cycle at switching potentials more negative than -1.25 V versus Ag/AgCl. This unusual behaviour was attributed to the reduction of 1-ethylpyridinium cations to pyridyl radicals and their follow-up reactions, which influenced the zinc electrochemistry. This behaviour was further seen to modify the nucleation process of electrodeposition, which altered the morphology of zinc electrodeposits.

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Introduction

The electrodeposition of metals commonly utilizes a variety of supporting electrolytes and additives to assist in the efficiency and quality of the electrodeposit. These various additives may be used to alter physical properties of the solution or to control the speciation of metal ions in order to influence deposition morphology.^[1–3] In the case of reversible electrodeposition for rechargeable flow batteries, these additives may enhance reoxidation of the metal to metal ions,^[4,5] or their functions may be extended to non-electrochemical functions that influence other chemistries in the cell.^[6–8]

An increasingly prevalent group of additives is a class of compounds called ionic liquids (IL), which are defined as salts that melt below 100°C.^[9] IL bromide salts, for example, are traditionally used in the zinc and vanadium bromide flow batteries, with 1-ethyl-1-methylpyrrolidinium bromide conventionally applied as a bromine sequestration agent.^[10–12] ILs have also been successfully applied as compounds capable of forming favourable complexes with metal ions to influence electrode-posit morphology.^[13,14] They can also possess wide electrochemical windows^[15] to allow the deposition of metals with low Nernst potentials, such as aluminium^[16] or magnesium.^[17]

Pyridinium-based ILs have shown promise as components of dye-sensitized solar cells and conductive polymers, and as additives for rechargeable battery cells.^[18,19] In the present work, we demonstrate their limits for use as electrolyte additives in zinc-containing cells. These insights are likely to extend to other metal-containing redox couples.

Results and Discussion

Cyclic Voltammetry

Fig. 1a shows cyclic voltammograms (CVs) for the 0.2 M KCl background electrolyte and for 50 mM 1-ethylpyridinium bromide ([C₂Py]Br) in the absence of zinc bromide at two different switching potentials. At a switching potential of -1.4 V, it is clear that a reduction of the $[C_2Py]Br$ occurs (onset at -1.25 V). This CV matches the electrochemical signal observed for the second and third CV cycle seen in the inset of Fig. 1b. Extending the switching potential for the [C₂Py]Br electrolyte reveals a peak current at -1.5 V, which is ascribed to the irreversible reduction of the 1-ethylpyridinium cation to a radical (Scheme 1), observed previously in aqueous solutions of pyridine.^[20] The electrochemical reduction of pyridine to pyridyl radicals is known to occur for neat alkylpyridinium ILs at -1.25 V versus Ag/AgCl,^[15,21] and has also been described in aqueous solutions of pyridine via a pyridinium intermedi-ate.^[20,22-24] In the present case, a direct and irreversible oneelectron reduction of the pyridinium cation's π -system is likely, as is observed for neat ILs.^[21] The observed crossover current in Fig. 1a is likely due to the grafting of the pyridical radical species on the electrode surface. The absence of a reoxidation process on the reverse scans is consistent with a rapid (on the cyclic voltammetric time scale) reaction of the radical, which is known to dimerize.^[25,26]

Fig. 1b shows three consecutive CVs for the Zn/Zn^{II} redox couple observed in equimolar (50 mM) solutions of zinc

^{*}Dedicated to Professor Alan Bond on the occasion of his 70th birthday - over 40 years of collaborations, distinguished and generous colleague and friend.



Fig. 1. Cyclic voltammograms performed at 100 mV s^{-1} on a glassy carbon working electrode in aqueous solutions of 0.2 M KCl supporting electrolyte: (a) in the absence of zinc bromide, showing the background scan for KCl and the irreversible reduction of 1-ethylpyridinium bromide onset at -1.25 V. (b) Zinc electrodeposition and stripping from an electrolyte containing zinc bromide (50 mM) and 1-ethylpyridinium bromide (50 mM) (inset is the expanded view of cycles 2 and 3).



Scheme 1. One-electron reduction of 1-ethylpyridinium (I, $[C_2Py]^+$) cations to 1-ethylpyridyl radicals (II, $[C_2Py]^{\bullet}$)

bromide and $[C_2Py]Br$ in 0.2 M KCl supporting electrolyte. The onset of zinc electrodeposition can be seen at -1.12 V, with a peak current of -0.25 mA reached at a potential of -1.20 V. Unexpectedly, two further reduction processes can be observed to begin at -1.30 and -1.38 V, before the switching potential of -1.40 V. On the return sweep to oxidizing potentials, zinc oxidation (stripping) begins at -1.03 V and two distinct oxidation processes can be observed with maxima at -0.95 and -0.84 V respectively. This suggests two distinct steps for the deposition and subsequent stripping of zinc in this system. Subsequent potential cycling results in a near-complete disappearance of signals assigned to the Zn/Zn^{II} redox couple (inset of Fig. 1b), with only the reduction at -1.4 V observed.

To further elucidate the role of reduced 1-ethylpyridinium cations in the voltammetric response observed in Fig. 1b, the switching potential was varied for a series of CV experiments (Fig. 2). When the first CV scan is reversed at -1.15, -1.20, and -1.25 V versus Ag/AgCl, conventional CV patterns for reversible metal electrodeposition are observed for both the first (Fig. 2a) and third (Fig. 2b) CV cycle. For those voltammograms recorded with switching potentials more negative than -1.30 V (beyond the observed onset potential for $[C_2Py]^+$ reduction, Fig. 1a), hydrogen generation and the development of a blue hue to the solution is noted. The zinc electrodeposition pattern is altered, with an additional reduction process observed. A shift in the onset of the oxidation voltage of zinc is observed (Fig. 2a) at switching potentials more negative than -1.30 V. This voltage shift is likely to be due to the grafting of the radical species onto the electrode surface, inhibiting the stripping of the electrodeposited zinc. A small oxidation process at a slightly more negative potential than that of the oxidative peak current at

-0.84 V is also observed. This demonstrates that the two distinct zinc redox processes are a result of the concurrent reduction of $[C_2Py]^+$ cations. On the third CV cycle, the previously described passivation of the zinc's electroactivity is seen only when zinc deposition occurs at potentials that also generate the proposed 1-ethylpyridyl radicals (Scheme 1).

The manner in which the formation of 1-ethylpyridyl radicals $([C_2Py]^{\bullet})$ affects zinc electrodeposition may be surmised from the experimental data. The additional deposition currents observed at -1.30 V occur only at potentials at which [C₂Py][•] radicals have been formed. The lack of Zn²⁺ reduction observed on subsequent scans may be due to numerous mechanisms. Most likely, the radical species generated can graft onto the electrode surface,^[27,28] preventing further Zn²⁺ reduction on subsequent cycles. The radical generated may also direct itself as a ligand for the divalent zinc ions in solution, forming, in the first instance, what could be assumed to be a complexed [Zn- $([C_2Py]^{\bullet})_n]^{2+}$ species. The stability of zinc complexes with radical ligands is well established.^[29–32] Any such species with presumed reduced charge density is likely to diffuse more slowly to the negatively polarized electrode (at reducing potentials) than do the divalent Zn^{2+} ions. This could explain the resultant second deposition signal that follows the direct reduction of Zn^{II} ions. After scanning to further reducing potentials and returning to oxidizing potentials, a sufficient amount of [C₂Py][•] radicals would have been generated to complex any zinc ions that were not electrodeposited on the time-scale of the CV experiment. The complexation of the zinc means the Zn²⁺ centre is thus unlikely to be reduced to electrodeposited metal at the potentials of these experiments, resulting in the passivation of zinc ions, as is observed in the CV study. However, [C₂Py][•] radicals are not the only complexing species that may be present.

Scheme 2 demonstrates possible reaction outcomes that may follow the electroreduction of 1-ethylpyridinium bromide in the investigated solutions. The noted colour change and evidence of hydrogen evolution suggest the dimerization of pyridyl radicals (II) to form the known neutral N,N'-diethyltetrahydro-4,4'-bipyridine compound (III)^[25,26] capable of coordinating metal ions through the lone pair electrons of one or both of its nitrogen atoms. In the presence of water, a dicationic viologen-type



Fig. 2. Cyclic voltammograms performed at 100 mV s^{-1} on a glassy carbon working electrode in aqueous solutions of zinc bromide (50 mM) and 1-ethylpyridinium bromide (50 mM) with KCl (0.2 M) as supporting electrolyte. The influence of switching potential on the Zn/Zn^{II} redox couple in the presence of 1-ethylpyridinium bromide is illustrated for: (a) the first CV cycle; (b) the third CV cycle. The switching potentials of the CV experiment are (top to bottom): -1.15, -1.20, -1.25, -1.30, -1.35, and -1.40 V versus Ag/AgCl.



Scheme 2. Possible reactions following the electrochemical formation of $[C_2Py]^{\bullet}$ (II, from Scheme 1) including: (2a) dimerization of two pyridyl radicals; (2b) formation of dicationic viologen-type dimer; (2c) further reduction of the dication to form vinylidene compound; and (2d) combination of IV and V to form cation–radical pair.

product is also capable of being formed (**IV**); however, owing to its positively charged nitrogen atoms, **IV** is less likely to coordinate Zn^{2+} ions. Instead, this compound can be further reduced to a neutral pyrilidene-type dimer **V** that may also act as a ligand in the complexation of zinc ions in a similar arrangement to that previously reported for the 1,1'-dihydro-4,4'bipyridyl complex.^[32] The dicationic species **IV** has been previously reported to subsequently react with **V** to form two molecules of the cation–radical compound **VI**, which may complex Zn^{II} via the radical site in a manner similar to that previously reported.^[33] It is also important to note that the Br⁻



Fig. 3. Spectral progression of $[C_2Py]Br (15 \text{ mM})$ at different potentials versus Ag/AgCl in KCl (0.1 mM) solution. The arrow indicates the direction of change of the spectral feature at more negative potentials.

ions from the starting bromide salt are common ligands for zinc, and are likely to be associated with zinc ions as bromozincates of the order of, for example, ZnBr₃^{-;[34,35]} however, this was not explored in the present work.

UV-vis spectroelectrochemistry was used to probe the formation of the proposed pyridine-containing complexes at different potentials (Fig. 3). At all potentials, an intense absorption at ~40000 cm⁻¹ was observed, which is ascribed to the pyridinium ring transition.^[36] Applying a negative potential of -1.0 V showed no change in the spectra. However, changing the negative potential to -1.2 V showed the formation of an additional absorption at ~31000 cm⁻¹. The intensity of this absorption band increased with the change in the applied 1028



Fig. 4. Chronoamperometric response for the potentiostatic deposition of zinc at various deposition potentials from an aqueous electrolyte comprising: zinc bromide (50 mM), 1-ethylpyridinium bromide (50 mM), and KCl (0.20 M).

potential from -1.2 to -1.4 V. The formation of this additional absorption is similar to that observed in the work of Wang et al.,^[36] who ascribed this absorption to the formation of a neutral pyrilidene-type dimer, as suggested in Scheme 2 (V). We also suggest that the pyridine-containing ligand may vary during the time-scale of the reducing potential scan.

Chronoamperometry

Fig. 4 shows the chronoamperometric response for the potentiostatic electrodeposition of zinc under various deposition potentials near the peak reductive current identified by CV. The influence of the presence or absence of pyridyl radical formation can be clearly seen in these chronoamperograms. On depositing at a constant potential of -1.20 V, the current response rapidly approaches a maximum of -250 µA, before a diffusion-controlled current decay for the short life time of the experiment (7 s). For potentiostatic depositions at -1.25 and -1.30 V, the maximum current is observed to be higher (owing to the greater overpotential delivered), reaching maximum currents of -370 and -420 µA respectively. Following the chronoamperometric current decay, additional steps in the current response can be observed at 4 and 2s respectively. This is consistent with the proposed additional deposition process, from, for example, the possible $(Zn-([C_2Py]^{\bullet})_n)^{2+}$ complex(es) or of complexes between Zn^{2+} and the products of radical dimerization, which are formed from the reduction of $[C_2Py]^+$ during electrodeposition at these higher overpotentials.

The appearance of chronoamperometric transients are a consequence of a nucleation-controlled initial process, followed by a current decay consistent with the diffusion of ions to the surface of the growing electrodeposit. Nucleation of metal sites can proceed by either an instantaneous or progressive mechanism of threedimensional island growth.^[37,38] For instantaneous nucleation, all nucleation sites are activated rapidly, resulting in evenly distributed growth sites. Progressive nucleation differs by a more gradual activation of nucleation sites, where clusters of metal deposits grow as other nucleation sites are activated. These theories of nucleation have been described by Scharifker and Hills,^[39] who derived mathematical models for both instantaneous (Eqn 1) and progressive nucleation mechanisms (Eqn 2). Although this model has limitations when used for complicated system such as that



Fig. 5. Normalized current responses and simulations using Scharifker–Hills nucleation models for the chronoamperograms of Fig. 3 at deposition potentials of: (a) -1.20 V; (b) -1.25 V; (c) -1.30 V.

outlined here, it provides a qualitative method for investigating the nucleation processes occurring in this system.

$$\left(\frac{i}{i_{\rm m}}\right)^2 = \frac{1.9542}{t/t_{\rm m}} \left\{1 - \exp[-1.2564(t/t_{\rm m})]\right\}^2$$
 (1)

$$\left(\frac{i}{i_m}\right)^2 = \frac{1.2254}{t/t_m} \left\{ 1 - \exp\left[-2.3367(t/t_m)^2\right] \right\}^2$$
(2)

By normalizing the experimental chronoamperogram to its current and time maxima (i.e. i_m and t_m), it can be compared with the theoretical transients defined by the relationships defined in



Fig. 6. SEM images for the electrodeposition of zinc (zinc bromide, 50 mM) in the presence of 1-ethylpyridinium bromide (50 mM) for 3 min on FTO glass, showing the influence of deposition potential on the resulting electrodeposit. Deposition potentials are: (a) -1.20 V; (b) -1.25 V; (c) -1.30 V.

Eqns 1 and 2. These mathematical models have been routinely utilized for the analysis of zinc electrodeposition.^[40–42] Fig. 5 shows the experimentally derived dimensionless plots of $(i/i_m)^2$ versus t/t_m compared with the theoretical transients for the diagnostic analysis of nucleation processes. When deposited at -1.20 V, a very good match to the predicted current transient for instantaneous nucleation is observed. This suggests that deposition at this potential will result in an evenly distributed zinc

electrodeposit, a postulate that was explored by scanning electron microscopy (SEM; see the section *Deposition Morphologies* below). At the more negative reducing potential of -1.25 V, however (Fig. 4b), the dimensionless chronoamperogram is observed to closely match the theoretical transient for progressive nucleation. Electrodeposition at -1.30 V is also consistent with a progressive nucleation process; however, the experimental transient fits the simulation of the simplified

mathematical model (which assumes, for example, spherical nucleation sites^[37]) less well.

The dimensionless chronoamperograms demonstrate that electrodeposition at more negative reducing potentials (concurrent with $[C_2Py]^{\bullet}$ formation) alters the nucleation process from an instantaneous to a progressive process, which gives a further indication of a secondary process of electrodeposition. Additional zinc electrodeposition processes have been previously observed in electrolyte media capable of complexing metal ions, such as ILs and related electrolytes.^[43-46]

Deposition Morphologies

In order to further examine the consequence of the differing current responses, electrodeposits were prepared via potentiostatic electrodeposition on a fluorine-doped tin oxide (FTO) glass substrate for 3 min. The zinc deposit morphology was examined by SEM, as seen in Fig. 6. Good uniform electrodeposits with deposits $<1 \,\mu m$ in diameter are obtained when zinc is electrodeposited at -1.20 V. This is to be expected of an instantaneous nucleation process followed by diffusion-controlled growth. However, when zinc is deposited at -1.25 V s^{-1} , disclike deposition morphology is observed in addition to the evenly distributed zinc, with features as large as 2 µm. This additional deposition morphology is consistent with the interpretations of the CV and chronoamperometric data, which indicate the presence of a second deposition process at significantly reducing potentials. As is to be expected, on depositing at -1.30 V, these disc-like features become much more prominent. The disc-like morphologies are seen to be larger ($\sim 4 \,\mu m$) and more widespread, perhaps due to the generation of a greater proportion of the possible intermediate species such as $[Zn-([C_2Py]^{\bullet})_n]^{2+}]$ and/or $[Zn(III)_n]^{2+}$, $[Zn(\hat{V})_m]^{2+}$, etc.

Conclusion

The unfavourable voltammetric behaviour observed for the Zn/ Zn^{II} redox couple in the presence of 1-ethylpyridinium bromide was ascribed to the influence of 1-ethylpyridyl radicals and/or their dimerization products that are formed electrochemically at potentials more negative than -1.25 V versus Ag/AgCl. Deposition of zinc at potentials more negative than this results in the predominance of a second, slow-nucleating deposition process that was observed to result in zinc deposits with large, disc-like morphologies by SEM. The complete passivation of zinc electroactivity on subsequent sweeps is proposed to be the result of either or both passivation of the electrode and complexation of Zn^{2+} ions by the reduction products of the IL cation. Thus, although the promise of alkylpyridinium IL salts has been outlined elsewhere, we have demonstrated a reducing potential limit of -1.25 V versus Ag/AgCl for metal deposition in the presence of such cations.

Experimental

Chemical Reagents

Zinc bromide dihydrate (ZnBr₂.2H₂O) was used as received (Aldrich). 1-Ethylpyridinium bromide ([C₂Py]Br) was prepared by quaternization of pyridine (Alfa-Aesar) with bromoethane (BDH) by standard literature methods.^[47] The resulting white solid was recrystallized from its acetonitrile solution by addition of ethyl acetate and was dried under vacuum at 60°C before use. FTO glass (TEC-15 glass plate, Dyesol Industries) was pre-treated by three rinses in a sonicating bath with acetone,

isopropanol, and deionized water sequentially. The treated FTO glass was dried under flowing nitrogen at room temperature before use.

Voltammetric Methods

All voltammetric experiments were performed on an edaq ER466 Integrated Potentiostat System (edaq, Australia) using a conventional three-electrode configuration. Cyclic voltammograms were obtained using a 1-mm diameter glassy carbon working electrode (edaq) with a Pt wire as counter-electrode and a leakless Ag/AgCl reference electrode (edaq). Potentials are reported relative to the Ag/AgCl reference electrode. Working electrodes were polished on a succession of alumina slurries (1 and 0.3 μ M) before each experiment and treated with oxidizing potentials following each experiment to remove any deposited zinc.

UV-vis spectroelectrochemistry was performed over the range of 20000–45000 cm⁻¹ using a Cary5000 spectrophotometer. The absorption spectra of the electrogenerated species was obtained in situ using a spectroelectrochemical cell mounted in the beam pathway of the spectrophotometer, with platinum mesh working and counter-electrodes and a Ag/AgCl reference electrode. Potentials were applied using an edaq ER466 Integrated Potentiostat System. Solutions were composed of [C₂Py] Br (15 mM) and a supporting electrolyte of KCl (0.1 M).

Chronoamperometry was performed in refreshed electrolyte solutions of identical compositions to those used in the cyclic voltammetric studies. Current-time transients were collected via two-step chronoamperometry, with 3-s equilibration time at -0.6 V preceding reduction at the required potential. Zinc electrodeposits were prepared on an FTO glass working electrode substrate by the same methodology. These electrodeposits were rinsed with deionized water and then acetone, before drying under flowing nitrogen at room temperature and mounting for SEM analysis. SEM was performed with a Zeiss ULTRA+ operating at 5.0 kV.

Conflicts of Interest

The authors declare no conflicts of interest.

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