Electrodeposition of lead from methanesulfonic acid and methanesulfonate ionic liquid derivatives

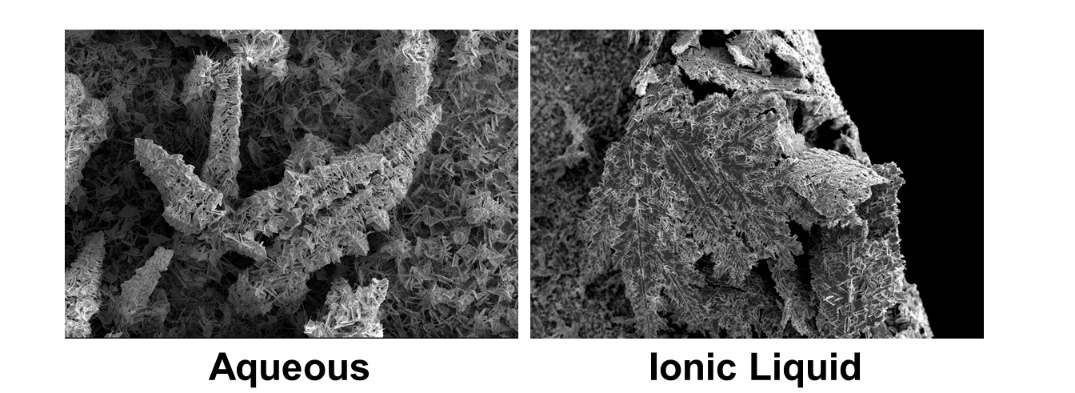
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**Abstract**

The influence is reported of electrolyte composition on the electrochemistry of PbII and electrodeposition morphology of Pb in aqueous methanesulfonic acid (MSA) and two methanesulfonate-based ionic liquids: 1-butyl-3-methylimidazolium methanesulfonate and *N,N*-dimethylbutylammonium methanesulfonate. Cyclic voltammetry and chronoamperometry indicated that the reduction of PbII ions to Pb was a diffusion-controlled process proceeding via a two-electron transfer process at -0.67 V vs. Ag (1 M MSA) and involved 3-D progressive nucleation. Scanning electron microscopy showed a strong influence of deposition potential and electrolyte composition on the morphology of Pb deposits. Experimental data was used to model predictions of the specific electrical energy consumption for cathodic PbII electrodeposition coupled with either anodic oxygen evolution or PbO2 electrodeposition.

**Graphical Abstract**



**Keywords**

Lead-acid battery recycling; Electrowinning; Lead; Methanesulfonic acid; Ionic Liquids

# Introduction

Continual growth in the production of vehicles and electric bicycles, all of which still employ lead-acid batteries (LABs), is linked directly to the increasing global lead demand of ca. 11.6 Mt a-1. This will unavoidably increase the production of spent LABs, which are highly recyclable, contributing > 85 % of secondary lead sources [1,2]. The most common route to secondary lead production from spent LABs is by direct smelting reduction, in which various lead oxides are reduced to metallic lead by carbon (coke and natural gas). Here, the high temperatures (1600 °C) required for smelting results in high energy consumptions and expensive gaseous and liquid pollution abatement technologies. Hence, low temperature hydro-metallurgical technologies based on lead electrowinning have been at the forefront of LAB recycling technology development, offering efficient and sustainable alternative processes [1,2].

Electrochemical processes for lead recovery from PbII can be carried out either in aqueous alkaline electrolytes such as sodium hydroxide [3–5], or aqueous acid electrolytes such as fluoroboric [6–10], nitric [11,12], acetic [13], chloride [14–19], etc. Nitric acid is unstable towards cathodic reductions and produce noxious atmospheres, while acetic acid has a strong odour and has a conductivity too low to allow economically viable operation of commercial electrochemical processes. Fluoroboric and hexafluorosilicic acids are used presently in commercial electrochemical processes for lead refining by the Betts process [20–22]. Both acids allow high PbII solubility (70 ­ 200 g dm-3) and high ionic conductivities. However, major problems associated with the use of fluorinated electrolytes include emissions of HF, fluoride­accelerated corrosion and difficulties in wastewater treatment.

Lead paste from LABs is a mixture of ‘PbSO4’ (50-60 wt%), PbO (5-10 wt%), PbO2 (15-35 wt%) and metallic Pb (2-5 wt%) [2,23] where ‘PbSO4’ refers to a range of phases such as PbO.PbSO4, PbSO4·PbO, PbSO4·2PbO, PbSO4·3PbO, PbSO4·4PbO and Pb(HSO4)2 all of which are used in the manufacturing of lead paste for LAB. Paste desulfurisation (1) is a vital step in the lead extraction process as ‘lead sulfate’ is essentially insoluble in acidic media. Hence, it is typically treated with Na2CO3 to convert it to PbCO3, while minimising dissolution as Pb(OH)3- ions at pH > 11 [24] prior to acid leaching (2).

Lead paste desulfurisation:

(1)

Acidic leaching:

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In acidic aqueous solutions, the standard equilibrium potential for the PbII/Pb couple is -0.126 V vs. SHE, but as lead has a high hydrogen overpotential, it can be electrodeposited with approaching unity charge yield.

The desired half-cell reactions are:

Cathode: ()

Anode: ()

While possible side reactions in an acidic electrowinning process are:

Cathode: ()

Anode: ()

In particular, compared to other acidic media, PbII in methanesulfonic acid (MSA) has a solubility of ca. 400 g dm-3 [25,26], enabling high electrodeposition current densities [27,28]. Furthermore, MSA is regarded as a ‘green’ solvent with mild corrosivity and is less toxic compared to fluoroboric and hexafluorosilicic acids, while also being non-volatile and having high ionic conductivity [29,30]. MSA has also been used as the electrolyte for the electrodeposition of various metals and alloys, such as copper [31], zinc [32], tin [33,34] and its alloys [31,35,36].

Additives are key to controlling the quality and morphology of electrodeposits. Typically, in additive-free electrolyte, lead deposits are highly dendritic. Inhibitors are required to increase the cathode deposition overpotential to produce smooth and dense deposits. Lignosulfonate salts have been investigated as additives in the Pb-MSA flow battery [37], leading to uniform deposition of lead with minimal dendrite formation [38]. However, the presence of lignosulfonate salts alone does not give adequate levelling benefits for the lead cathode, so other additives such as animal glue, aloin and chestnut extract are required to maintain acceptable deposit morphologies [39]. The effect of organic additives on the morphology of electrodeposited Pb [40,41] and Pb-based alloys [42,43] from methanesulfonate electrolytes have also been reported.

Despite extensive research since the 1980s that led to numerous piloted technologies in lead recovery from spent LABs, it is difficult to avoid dendritic growth of lead on cathodes. In recent years, room temperature ionic liquids (RTILs) have been investigated as alternative electrolytes for lead electrodeposition, utilising their unique electrochemical properties such as wide solvent potential windows, high thermal stabilities and high ionic conductivities. Furthermore, ionic liquids have been shown to alter surface layer structures of electrode│electrolyte interfaces, suppressing dendrite formation in zinc [44,45] and lithium [46,47] deposition for battery applications, possibly obviating the need for additives and levellers in electrolyte design.

With the objectives of understanding the effect of IL composition on the electrochemistry and electrodeposition morphology of lead, we investigated the electrodeposition of PbII from an imidazolium-based IL, 1-butyl-3-methylimidazolium methanesulfonate, [BMIM][MS]. Imidazolium-based ILs are known typically for their non-volatility, relatively high conductivity, low viscosity and hydrophilicity. These characteristics could be particularly beneficial in prospective lead recovery processes, in which water is present necessarily and could be added intentionally to decrease viscosities and increase ionic conductivities of electrolyte solutions. Moreover, an imidazolium-based IL containing methanesulfonate anions would be less toxic compared to the fluorine-based anions typically employed.

Thermo-physical properties for a range of imidazolium based IL-water binary systems have been reported [48–50]. Paul et al measured the solution behaviour of [BMIM][MS] in water over a wide range of concentrations and reported a linear dependence of molar conductance on solution viscosity in a Walden plot [50]. Conductivities (3 S m-1 at 1.0 M) and viscosities (2 mPa s at 1.0 M) suitable for the applications discussed herein were also reported [50]. Solvent potential windows were also reported for the IL-water binary mixture, showing a potential limit due to solvent reduction suitable for lead electrodeposition [50].

Cost is a central issue impeding the development of industrial processes that utilise ILs [51,52]. Herein, we also investigate the electrochemical recovery of Pb from a low-cost protic IL based on a simple amine: *N,N*-dimethylbutylammonium methanesulfonate, [DMBA][MS]; toxicity of this IL-water mixture is expected to be similar to that of the parent amine and acid. Amine toxicity is dependent on the chain length, with longer alkyl chains increasing toxicity, so shorter alkylamines are to be preferred[51]. To the best of our knowledge, this is the first report of [DMBA][MS], so its thermo-physical properties have not been available hitherto and will be explored further in future studies.

The electrochemistry and electrodeposition of PbII from both IL-water binary mixtures are compared to that of MSA electrolyte as a model system, the behaviour of which has been reported extensively [25,38]. In this study, we explore the use of ILs to control/obviate dendritic lead grown which is a general problem encountered with electrochemical lead recovery.

# Experimental

## Preparation of solutions

Solutions of 1.0 M methanesulfonic acid (MSA) (99.0 %, Merck) and 1.0 M 1-butyl-3-methylimidazolium methanesulfonate, [BMIM][MS], (99.0 %, IoLiTec) + 1.0 M MSA were prepared using water, purified with a Millipore Milli-Q purification system (resistivity ca. 18.2 MΩ cm at 25 °C). A protic ionic liquid, *N,N*-dimethylbutylammonium methanesulfonate, [DMBA][MS], was synthesised by combining *N,N*-dimethlybutylamine (99.0 %, Merck) with MSA in a stoichiometric (base to acid mole ratio) of 1:2, denoted as [DMBA][MS] 1:2 herein. The reaction is shown in Scheme S1 in the Supporting Information (SI). This was achieved by dropwise addition of MSA (5.0 M) to DMBA in a round-bottom flask placed in an ice bath. As the reaction was exothermic, the mixture was stirred for several hours until it cooled to room temperature [51]. The formation of the ionic liquid was confirmed by nuclear magnetic resonance (NMR) spectroscopy recorded on a Bruker Avance-400 (1H NMR (400 MHz)) NMR spectrometer. Spectra and chemical shifts are reported in the SI, Figure S1. Water was then added to obtain a solution of 50 wt% water confirmed by Karl Fischer (Volumetric, Mettler Toledo). PbII solutions were prepared by dissolution of lead (II) carbonate, PbCO3, as the lead source, in the respective electrolyte mixtures.

## Electrochemistry and electrodeposition experiments

Electrochemical measurements were made using a potentiostat (Autolab PGSTAT30) and NOVA software. A glassy carbon (GC) disc electrode (3.0 mm diameter) served as the working electrode in all cyclic voltammetry and chronoamperometry experiments. Prior to use, the working electrode was polished with a slurry of 0.05 μm alumina particles on a soft microfibre polishing pad (MicroCloth, Buehler Ltd.) and then on a clean wet microfibre pad. A platinum gauze acted as the counter electrode. A quasi-reference electrode (QRE) was used and comprised a Ag wire inserted into a glass tube fritted with CoralPorTM (7.8 nm pore size). The glass tube was filled with 1.0 M MSA solution and had a stable potential of 0.510 V vs SHE. All electrochemical experiments were carried out at ambient temperature (293 ± 2 K).

The key performance indicators of the electrodeposition process were the charge yield, , and the specific electrical energy consumption,, calculated from:

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where andrepresent the anodic and cathodic charge passed during the positive-going and negative-going potential sweeps, respectively, *F* represents the Faraday constant, *M*Pb the molar mass of lead and *U* the cell potential difference.

Electrodeposition experiments were conducted with a copper foil (Goodfellow, 99.9%) substrate and a lead wire (Goodfellow, 99.99%, As (0.3 ppm), Bi (2.1 ppm), Cu (0.3 ppm) and Ag (0.9 ppm)) acting as the working electrode and counter electrode, respectively. After electrodeposition, the samples were washed with distilled water to remove residual electrolyte from the sample surface and were subsequently dried in air before characterisation. The surface morphology of the lead deposits on copper foil were imaged with scanning electron microscopy (JOEL 6010A) coupled with energy dispersive X-ray spectroscopy to provide elemental composition of the samples.

# Results and Discussion

## Voltammetry

Figure 1 shows 5 repetitive cyclic voltammograms (0.05 V s-1) of a GC electrode in 25×10-3 M PbII in (a) MSA, (b) [BMIM] [MS] + MSA and (c) [DMBA][MS] 1:2, 50 wt% H2O. The current response to the initial negative-going potential scan from the start potential of -0.30 V vs. Ag (1 M MSA), was a reduction wave and peak followed by typical diffusion controlled current decay. In Figure 1(a), these were detected on the first potential scan at ­0.725 V vs. Ag and corresponded to electrodeposition of Pb via an overall two-electron transfer reaction (3). On the subsequent positive-going potential scan from the negative potential limit, the cathodic current density decreased progressively, became anodic at potentials > ­0.676 V vs. Ag, and an oxidative stripping peak occurred at ­0.585 V vs. Ag corresponding to dissolution of the Pb electrodeposited from the previous negative-going potential scan. Current densities approached zero at potentials less negative than that corresponding to the peak potential, indicating complete/close to complete oxidative dissolution of metallic Pb. The potential, *EI*=0, at which current, *I* = 0, on the positive-going potential scan was ­0.676 V vs. Ag and is the estimated formal potential for the PbII/Pb couple in 25×10-3 M PbII + 1.0 M MSA. These voltammograms are consistent with previous reports [25,38] of the electrochemical behaviour of PbII in aqueous MSA media.



Figure 1. Cyclic voltammograms at 0.05 V s-1 from repetitive potential cycling of a GC disc electrode in 25×10-3 M PbCO3 in (a) 1 M MSA, (b) 1 M [BMIM][MS] + 1 M MSA and (c) [DMBA][MS]. The potential scan ranged from -0.3 to -1.1 V vs. Ag (1 M MSA).

As expected, a large overpotential was evident and associated with the nucleation of Pb on GC. On repetitive potential cycling (Figure 1(a)), the reductive peak potential of Pb deposition shifted monotonically toward less negative (driving) potentials, while the oxidative stripping peak remained relatively unchanged (values reported in SI, Table S1). The ratio of charges for dissolution and deposition, was 0.93 on the first voltammetric scan, but increased to ca. 0.96 after 5 scan cycles. This suggested the longevity of Pb nuclei on the GC electrode that were not removed totally during Pb dissolution on the subsequent positive-going potential sweep [53], which facilitated fast Pb on Pb deposition kinetics.

For comparison, Figure 1(b) and (c) show the electrochemical behaviour of 25×10-3 M PbII in [BMIM][MS] and [DMBA][MS], respectively. The general electrochemical behaviour of PbII in both IL media are similar to that of PbII in MSA. However, reduction peak potentials for Pb deposition were determined as ­0.754 V and ­0.743 V in [BMIM][MS] and [DMBA][MS], respectively, compared to ­0.725 V for MSA, suggesting kinetic limitations in the nucleation of Pb on GC in both IL-H2O mixtures studied. As found in MSA media, repetitive potential cycling caused the reductive peak potential to shift to less negative values, ­0.741 V and ­0.709 V for [BMIM][MS] and [DMBA][MS], respectively, revealing slow formation of Pb nucleation sites on the GC electrode surface on the initial negative-going potential scan, followed by fast Pb on Pb deposition on subsequent potential scans (shown in Figure 1 insets). The values of 160 mV and 134 mV for the potential separations, of cathodic-anodic current peaks for [BMIM][MS] and [DMBA][MS], respectively, suggested Pb deposition was faster in [DMBA][MS].

Figure 2(a), (b) and (c) show cyclic voltammograms at 0.05 V s-1 for the reduction of PbII at a GC electrode in MSA, [BMIM][MS] and [DMBA][MS], respectively, for PbII concentrations of (5, 10, 15, 20 and 25) ×10-3 M. As the concentration of PbII was increased, the PbII/Pb formal potential shifted positively and changed linearly with the logarithm of PbII concentration by ca. 28 mV per 10-fold concentration change, as expected for the 2-electron transfer reaction (3).



Figure 2. Cyclic voltammograms at 0.05 V s-1 of a GC disc electrode in (*c* = 5, 10, 15, 20 and 25) ×10-3 M PbCO3 in (a) 1.0 M MSA, (b) 1.0 M [BMIM][MS] + 1.0 M MSA and (c) [DMBA][MS] 1:2, 50 wt% H2O. The potential scan ranges from -0.3 to -1.1 V vs. Ag (1.0 M MSA). Data shown were taken from first scan voltammograms of freshly polished GC electrodes.

## Chronoamperometry

Chronoamperometry was used to elucidate the nucleation and growth mechanism of Pb electrodeposition from PbII in the various electrolyte solutions onto GC electrodes, by stepping the electrode potential. Figure 3(i) shows the resulting current transients obtained for Pb deposition from 25×10-3 M PbII in (a) MSA, (b) [BMIM][MS] + MSA and (c) [DMBA][MS] 1:2, 50 wt% H2O for a range of step potentials.

Typical nucleation and growth current transients were characterised by an initial increase in current to a maximum, *I*max, at time, *t*max, followed by transient decay due to the increasing diffusion layer thickness and overlap of nucleation sites, so decreasing rates of atom incorporation into growing crystal lattices. For all PbII solutions studied, a decrease in *t*max and an increase of *I*max occurred with increasing applied deposition overpotential, attributed to increased nucleation rates and densities, values for which are listed in Table S4 of the SI.

At longer times, currents converged and followed the behaviour predicted by the Cottrell equation (9), enabling diffusion coefficients of the dissolved PbII species in all 3 solvent systems to be determined:

(9)

where represents the current density transient and time.

The diffusion coefficients of PbII were found to be 5.7 ± 0.6 × 10-10, 4.1 ± 0.6 × 10-10 and 2.9 ± 0.1 × 10-10 m2 s-1 in MSA, [BMIM][MS] and [DMBA][MS], respectively. These values are in good agreement with values calculated from cyclic voltammetric data (Section 3.1).



Figure 3. (i) Effects of time, *t*, and electrode potential on current, *I*, for GC disc electrode in 25×10-3 M PbCO3 in (a) 1 M MSA, (b) 1 M [BMIM][MS] + 1 M MSA and (c) [DMBA][MS] 1:2, 50 wt% water. (ii) Comparison of dimensionless experimental *I*-*t* data and theoretically predicted data for 3-D instantaneous (black) and progressive (red) nucleation under diffusion-controlled growth.

The nucleation growth mechanism of metals onto a different substrate typically follow 3-D nucleation that can be described by a dimensionless time-dependent current model [54,55] which describes two limiting mechanisms of nucleation: instantaneous and progressive. Instantaneous nucleation describes the formation of nuclei at the early stages after application of the driving potential step when the number of nuclei remain fixed, with further deposition occurring via growth of existing nuclei. In the case of progressive nucleation, new nuclei can form at any time during the potential step concurrently with nuclei growth. Hence, with each nucleus defining its own diffusion zone, a system with constantly forming nuclei will produce a different current (diffusion) profile to a system with a fixed number of nuclei. The dimensionless time-dependent current profiles for two limiting cases, instantaneous and progressive nucleation processes are given by (10) and (11), respectively [54].

Instantaneous nucleation: (10)

Progressive nucleation: (11)

Figure 3(ii) shows a comparison between experimental and theoretical *I*-*t* transients for the deposition of Pb on a GC electrode in (a) MSA, (b) [BMIM][MS] and (c) [DMBA][MS]. For MSA and [BMIM][MS] electrolyte, it is evident that a progressive nucleation mechanism occurred for all deposition potentials investigated. However, in [DMBA][MS], clear progressive nucleation was evident only at deposition potentials < -0.74 V. At less negative deposition potentials, an intermediate behaviour was operative, that may have been due to mixed kinetic-diffusion control, leading to a sub-linear time-dependent progressive nucleation mechanism [56,57].

## Deposition morphology

Figure 4 shows SEM images of Pb electrodeposits on Cu foil substrates from 25×10-3 M PbII in 1 M MSA at overpotentials of (a) -30 mV, (b) -100 mV and (c) -220 mV for 1 h. At -30 mV overpotential, the deposition reaction was kinetically-limited, and the crystal growth rate was slow, producing a smooth granular morphology with grain sizes 5-10 μm. At -100 mV overpotential, the Pb crystal growth rate was mass transport limited and dendritic flakes were evident uniformly distributed across the electrode surface. At -220 mV, a porous dendritic flake structure was evident, due to the hydrogen evolution reaction (5) causing adhering bubbles on the electrode surface [58].



Figure 4. SEM images of Pb deposits obtained at room temperature on Cu foil substrates from 25 × 10-3 M PbCO3 in 1 M MSA after 1 h at deposition overpotentials of (a) -30 mV, (b) -100 mV and (c) -220 mV.

Figure 5 shows SEM images comparing Pb deposits on Cu foil substrates from: (a) MSA, (b) [BMIM][MS] + MSA and (c) [DMBA][MS] 1:2, 50 wt% H2O, at a deposition overpotential of -100 mV for 2 h. A strong influence of electrolyte composition on deposition morphology was evident. The Pb deposits from MSA and [BMIM][MS] both exhibited dendritic structures with a flake-like and tubular morphology, respectively, while from [DMBA][MS] 1:2, 50 wt% H2O, a smooth leaf-like deposition morphology was observed. EDX analysis (Figure 5(d)) of the electrodeposits produced at -100 mV overpotentials in MSA electrolyte showed peaks corresponding only to Pb and the Cu substrate as expected.



Figure 5. SEM images of Pb deposits obtained on Cu foil substrates from 25 × 10-3M PbCO3 in (a) 1 M MSA, (b) 1 M [BMIM][MS] + 1 M MSA and (c) [DMBA][MS] 1:2, 50 wt% H2O, at a deposition overpotential of -100 mV for 2 h. (d) EDX spectra of Pb electrodeposits from 25×10-3 M PbCO3 in 1 M MSA.

## Microkinetic modelling

As shown in Figure 6, the potential dependencies of current densities and charge yields for Pb electrodeposition at GC electrodes in MSA, [BMIM][MS] and [DMBA][MS] were determined from experimental data. As expected, there was little to no effect of Pb deposition potential on the transport limited current density in the potential range of -0.72 to -1.0 V in the [BMIM][MS] and [DMBA][MS] IL electrolyte mixtures. This results in consistently high charge yield of ca. 0.96 and 0.92 for [BMIM][MS] and [DMBA][MS], respectively. At potentials <-0.7 V, the Pb deposition reaction is kinetically limiting and reduced charge yields are observed. In MSA electrolyte, the current density increases at Pb deposition potentials more negative than -0.95 V due to contributions from hydrogen evolution (5). At Pb deposition potentials between -0.7 and -0.95 V, consistently high charge yields of ca. 0.97 are observed while at -1.0 V, the charge yield falls slightly to 0.91.



Figure 6. Effect of electrode potential on current densities and charge yields for Pb deposition from 25×10-3 M PbII in 1 M MSA (), 1 M [BMIM][MS] + 1 M MSA () and [DMBA][MS] 1:2, 50 wt% water ().

### Case 1: Modelled system with oxygen evolution as the anodic reaction

Together with experimental data presented above for the PbII cathodic reduction reaction (3), the oxygen evolution reaction (4) on iridium oxide (IrOx) in acidic media was modelled as the anodic reaction of interest to predict the specific electrical energy consumption (SEEC),. An exchange current density, = 1.6 × 10-9 A m-2, [59] at pH = 2 (Na2SO4 and H2SO4 solution), was taken from literature as a suitable approximation for all 3 electrolyte solutions considered. We note that convective effects from bubble evolution were not considered. It was also assumed that excess supporting electrolyte minimised migrational contributions to overall transport rates and a charge yield of unity applied to the oxygen evolution reaction. Furthermore, it was envisaged that anodically generated oxygen would result in current efficiency losses at the cathode due to the reduction of dissolved oxygen, so a cation-permeable membrane (Nafion, conductivity, = 4.5 S m-1) [60] notionally was required to separate anolyte and catholyte. The use of a membrane also enabled the anolyte to be PbII-free, mitigating the possibility of PbO2 deposition at the anode by reaction (6).

The cell potential difference, , was calculated from:

(12)

where is the current. , and are the cross-sectional area, current path length and conductivities of , respectively. represents the catholyte, anolyte or membrane. is given by experimentally applied cathodic potentials while is calculated from the following, assuming kinetic control only:

(13)

where is the Tafel slope corresponding to 0.029 V dec-1 [59].

The SEEC for Pb recovery was predicted from (8) and the results are shown in Figure 7a(i) and (ii) for a range of cell potential differences and current densities, respectively. For cell potential differences of 1.75 to 2.05 V, there was little change in the SEEC values which have an average of 488, 494 and 512 kW h tPb-1 for MSA, [BMIM][MS] and [DMBA][MS], respectively. For a specific energy cost of $0.05 (kW h)-1, this translates to specific electrical energy costs of $24.40, $24.70 and $25.60 tPb-1 respectively, for MSA, [BMIM][MS] and [DMBA][MS], compared to LME prices (accessed 25 March 2020) of ca. $1,589 tPb-1. Note that the experimental PbII concentration is low for an industrial process. An estimation of the SEECs for molar concentrations of PbII in MSA, [BMIM][MS] and [DMBA][MS] gives average values of 694, 687 and 730 kW h tPb-1, respectively, due to increased ohmic effects.





Figure 7. Effects of (i) cell potential differences and (ii) current density on the SEECs for (a) Pb deposition coupled with oxygen evolution on IrOx and (b) simultaneous Pb and PbO2 deposition from 25×10-3 M PbCO3 in 1 M MSA (), 1 M [BMIM][MS] + 1 M MSA () and [DMBA][MS] 1:2, 50 wt% water ().

### Case 2: Modelled system with lead dioxide deposition as the anodic reaction

The model was extended to consider the simultaneous deposition of Pb at the cathode and PbO2 at the anode in a membrane-less reactor. Chronopotentiometry experiments were carried out at a GC electrode in solutions of 25 ×10-3 M PbCO3 in 1 M MSA, 1 M [BMIM][MS] + 1 M MSA and [DMBA][MS] 1:2, 50 wt% water at anodic current densities corresponding to current values observed for Pb deposition. The resulting deposition potentials and charge yield for PbO2 deposition are calculated and used within the model. The data is tabulated in the SI, Table S5. The SEEC formula for Pb recovery is amended to account for additional Pb removed in the form of PbO2 and is given by:

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Figure 7(b) summaries the SEEC for the simultaneous deposition of Pb and PbO2. Typical values of SEEC for Pb recovery from MSA is found to be ca. 172 . This value is lower than that for [BMIM][MS] and [DMBA][MS] at ca. 198 and ca. 180 , respectively.

Deployment of oxygen evolution reaction at the anode has been a typical strategy for piloted Pb electrowinning technologies such as FLOBUR [9,10] and PLACID [15,16] processes. However, as shown herein, lower SEEC values are predicted for simultaneous Pb and PbO2 deposition, even though larger cell potentials are required due to the additional PbO2 product stream. We note the electrochemical stability of [BMIM][MS] and [DMBA][MS] at such anode potentials are not known [50,61], but will be reported in the future.

# Conclusions

Pb was electrodeposited easily from PbII containing methanesulfonic acid media and 2 associated ILs, 1-butyl-3-methylimidazolium methanesulfonate and *N,N*-dimethylbutylammonium methanesulfonate, via an overall two-electron process. Higher overpotentials were needed for both IL electrolyte systems compared to the acid solution. The diffusion coefficients for PbII were found to decrease in the order: MSA > [BMIM][MS] > [DMBA][MS]. For all three electrolyte solutions, 3D-progressive nucleation occurred with diffusion-controlled growth. SEM images of Pb deposits on Cu foil substrates exhibited highly dendritic Pb morphology from MSA and [BMIM][MS], while a smoother deposit was evident from [DMBA][MS]. Potential-dependent deposit morphologies were produced from (aqueous) MSA solutions and will be investigated further for both IL electrolyte solutions.

Methanesulfonate-based ILs offer a promising commercial electrolyte for electrochemical recovery of Pb from spent lead acid batteries. As reported herein, charge yields > 0.96 were achieved with moderate SEEC within the range of 170-510 kW h tPb-1 when comparing modelled data for two possible anode reactions: oxygen evolution and lead dioxide deposition. Furthermore, as the use of different IL cations led to highly contrasting Pb deposition morphologies at the same deposition conditions, systematic variation of the IL cation would be expected to have dramatic effects on the Pb deposition morphologies from the IL-methanesulfonate electrolyte. The role of ILs in obviating the use of organic additives and levellers in electrolyte design would be welcomed in the development of LAB recycling technologies.

# Acknowledgements

The authors thank the UK Engineering and Physical Sciences Research Council for grant EP/P004504/1 providing a research associateship for S.T.

# References

[1] W. Zhang, J. Yang, X. Wu, Y. Hu, W. Yu, J. Wang, J. Dong, M. Li, S. Liang, J. Hu, R.V. Kumar, A critical review on secondary lead recycling technology and its prospect, Renew. Sustain. Energy Rev. 61 (2016) 108–122.

[2] S. Tan, D.J. Payne, J.P. Hallett, G.H. Kelsall, Developments in electrochemical processes for recycling lead–acid batteries, Curr. Opin. Electrochem. 16 (2019) 83–89.

[3] N.P. Brandon, D. Pilone, G.H. Kelsall, Q. Yin, Simultaneous recovery of Pb and PbO2 from battery plant effluents. Part II, J. Appl. Electrochem. 33 (2003) 853–862.

[4] S.M. Wong, L.M. Abrantes, Lead electrodeposition from very alkaline media, Electrochim. Acta. 51 (2005) 619–626.

[5] C. Frias, N. Ocaña, G. Diaz, T. Piper, B. Bulkowski, A. Chmielarz, P. Claisse, S. Hemmings, L. Abrantes, H. Jansen, J. Van Erkel, T. Franken, Z. Kunicky, T. Velea, a Clean-Lead Factory Is Available for Lead-Acid Batteries Recycling By Means of the “ Cleanlead Process ,” (2005) 943–951.

[6] R. David Prengaman, R.D. Prengaman, Recovering Lead from Batteries, JOM. 47 (1995) 1–2.

[7] A.Y. Lee, E.R. Cole, D.L. Paulson, Electrolytic methods for recovery of lead from scrap batteries, (1984).

[8] M. Olper, M.G. Maccagni, Pb Battery Recycling. New Frontiers in Paste Desulphurisation and Lead Production, (2008) 237–246.

[9] M. Olper, M. Maccagni, C.J.N. Buisman, C.E. Schultz, Electrowinning of Lead Battery Paste with the Production of Lead and Elemental Sulphur Using Bioprocess Technologies, in: Lead-Zinc 2000, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2013: pp. 803–814.

[10] F. Ojebuoboh, S. Wang, M. Maccagni, Refining primary lead by granulation-leaching-electrowinning, JOM. 55 (2003) 19–23.

[11] N.D. Nikolić, K.I. Popov, P.M. Živković, G. Branković, A new insight into the mechanism of lead electrodeposition: Ohmic-diffusion control of the electrodeposition process, J. Electroanal. Chem. 691 (2013) 66–76.

[12] N.D. Nikolić, G. Branković, U.C. Lačnjevac, Formation of two-dimensional (2D) lead dendrites by application of different regimes of electrolysis, J. Solid State Electrochem. 16 (2012) 2121–2126.

[13] E. Ghali, M. Girgis, Electrodeposition of lead from aqueous acetate and chloride solutions, Metall. Trans. B. 16 (1985) 489–496.

[14] E. Expósito, J. Iniesta, J. González-García, V. Montiel, A. Aldaz, Lead electrowinning in an acid chloride medium, J. Power Sources. 92 (2001) 260–266.

[15] G. Díaz, D. Andrews, Placid—A clean process for recycling lead from batteries, JOM. 48 (1996) 29–31.

[16] G. Díaz, D. Martín, C. Frías, F. Sánchez, Emerging applications of ZINCEX and PLACID technologies, JOM. 53 (2001) 30–31.

[17] D. Andrews, A. Raychaudhuri, C. Frias, Environmentally sound technologies for recycling secondary lead, (2000) 124–129.

[18] M. Maccagni, New Approaches on Non Ferrous Metals Electrolysis, Chem. Eng. Trans. 41 (2014) 61–66.

[19] M. Maccagni, S. Cossali, C. Roncaldier, C. Olper, L. Olper, A. Olper, Process for producing metallic lead starting from desulfurized pastel, 12/745,067, 2008.

[20] J.A. González-Domínguez, E. Peters, D.B. Dreisinger, The refining of lead by the Betts process, J. Appl. Electrochem. 21 (1991) 189–202.

[21] T. Dobrev, S. Rashkov, Processes during the electrorefining and electrowinning of lead, Hydrometallurgy. 40 (1996) 277–291.

[22] J.J. Fingland, The Betts Electrolytic Lead Refining Process in Practice, J. Electrochem. Soc. 57 (1930) 177–204.

[23] R.D. Prengaman, A.H. Mirza, Recycling concepts for lead–acid batteries, in: Lead-Acid Batter. Futur. Automob., Elsevier, 2017: pp. 575–598.

[24] K.J. Powell, P.L. Brown, R.H. Byrne, T. Gajda, G. Hefter, A.-K. Leuz, S. Sjöberg, H. Wanner, Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: The Pb2+ + OH–, Cl–, CO32–, SO42–, and PO43– systems (IUPAC Technical Report), Pure Appl. Chem. 81 (2009) 2425–2476.

[25] D. Pletcher, R. Wills, A. Hazza, A novel flow battery: A lead acid battery based on an electrolyte with soluble lead(ii), Phys. Chem. Chem. Phys. 6 (2004) 1773.

[26] M.D. Capelato, J.A. Nóbrega, E.F.A. Neves, Complexing power of alkanesulfonate ions: the lead-methanesulfonate system, J. Appl. Electrochem. 25 (1995) 408–411.

[27] V.S. Protsenko, E.A. Vasil’eva, F.I. Danilov, Electrodeposition of lead coatings from a methanesulphonate electrolyte, J. Chem. Technol. Metall. 50 (2015) 39–43.

[28] J. Dong, X. Wu, Y. Chen, N. Brandon, X. Li, J. Yang, J. Yu, W. Zhang, Y. Hu, W. Yu, J. Wang, S. Liang, J. Hu, H. Hou, B. Liu, C. Yang, A study on Pb2+/Pb electrodes for soluble lead redox flow cells prepared with methanesulfonic acid and recycled lead, J. Appl. Electrochem. 46 (2016) 861–868.

[29] F.C. Walsh, C. Ponce de León, Versatile electrochemical coatings and surface layers from aqueous methanesulfonic acid, Surf. Coatings Technol. 259 (2014) 676–697.

[30] M.D. Gernon, M. Wu, T. Buszta, P. Janney, Environmental benefits of methanesulfonic acid, Green Chem. 1 (1999) 127–140.

[31] C.T.J. Low, F.C. Walsh, Electrodeposition of tin, copper and tin-copper alloys from a methanesulfonic acid electrolyte containing a perfluorinated cationic surfactant, Surf. Coatings Technol. 202 (2008) 1339–1349.

[32] P.K. Leung, C. Ponce-De-León, C.T.J. Low, F.C. Walsh, Zinc deposition and dissolution in methanesulfonic acid onto a carbon composite electrode as the negative electrode reactions in a hybrid redox flow battery, Electrochim. Acta. 56 (2011) 6536–6546.

[33] I.S. Zavarine, O. Khaselev, Y. Zhang, Spectroelectrochemical study of the effect of organic additives on the electrodeposition of tin, J. Electrochem. Soc. 150 (2003) 202–207.

[34] Y.H. Yau, Effect of process variables on electrotinning in a methanesulfonic acid bath, J. Electrochem. Soc. 147 (2000) 1071–1076.

[35] N. Pewnim, S. Roy, Electrodeposition of tin-rich Cu–Sn alloys from a methanesulfonic acid electrolyte, Electrochim. Acta. 90 (2013) 498–506.

[36] C.T.J. Low, F.C. Walsh, Normal and anomalous electrodeposition of tin–copper alloys from methanesulphonic acid bath containing perfluorinated cationic surfactant, Trans. IMF. 86 (2008) 315–325.

[37] A. Hazza, D. Pletcher, R. Wills, A novel flow battery—A lead acid battery based on an electrolyte with soluble lead(II), J. Power Sources. 149 (2005) 103–111.

[38] Z. Wu, D.B. Dreisinger, H. Urch, S. Fassbender, Fundamental study of lead recovery from cerussite concentrate with methanesulfonic acid (MSA), Hydrometallurgy. 142 (2014) 23–35.

[39] B. Jin, D.B. Dreisinger, A green electrorefining process for production of pure lead from methanesulfonic acid medium, Sep. Purif. Technol. 170 (2016) 199–207.

[40] D. Pletcher, H. Zhou, G. Kear, C.T.T.J. Low, F.C. Walsh, R.G.A.A. Wills, A novel flow battery-A lead-acid battery based on an electrolyte with soluble lead(II). V. Studies of the lead negative electrode, J. Power Sources. 180 (2008) 621–629.

[41] A. Hazza, D. Pletcher, R. Wills, A novel flow battery—A lead acid battery based on an electrolyte with soluble lead(II), J. Power Sources. 149 (2005) 103–111.

[42] F.I. Danilov, V.S. Protsenko, E.A. Vasil’eva, O.S. Kabat, Antifriction coatings of Pb-Sn-Cu alloy electrodeposited from methanesulphonate bath, Trans. Inst. Met. Finish. 89 (2011) 151–154.

[43] F.I. Danilov, E.A. Vasil’eva, T.E. Butyrina, V.S. Protsenko, Electrodeposition of lead-tin alloy from methanesulphonate bath containing organic surfactants, Prot. Met. Phys. Chem. Surfaces. 46 (2010) 697–703.

[44] Z. Liu, T. Cui, G. Pulletikurthi, A. Lahiri, T. Carstens, M. Olschewski, F. Endres, Dendrite-Free Nanocrystalline Zinc Electrodeposition from an Ionic Liquid Containing Nickel Triflate for Rechargeable Zn-Based Batteries, Angew. Chemie - Int. Ed. 55 (2016) 2889–2893.

[45] Z. Liu, G. Pulletikurthi, A. Lahiri, T. Cui, F. Endres, Suppressing the dendritic growth of zinc in an ionic liquid containing cationic and anionic zinc complexes for battery applications, Dalt. Trans. 45 (2016) 8089–8098.

[46] J.K. Stark, Y. Ding, P.A. Kohl, Dendrite-free electrodeposition and reoxidation of lithium-sodium alloy for metal-anode battery, J. Electrochem. Soc. 158 (2011) 1100–1105.

[47] N. Schweikert, A. Hofmann, M. Schulz, M. Scheuermann, S.T. Boles, T. Hanemann, H. Hahn, S. Indris, Suppressed lithium dendrite growth in lithium batteries using ionic liquid electrolytes: Investigation by electrochemical impedance spectroscopy, scanning electron microscopy, and in situ 7Li nuclear magnetic resonance spectroscopy, J. Power Sources. 228 (2013) 237–243.

[48] W. Liu, T. Zhao, Y. Zhang, H. Wang, M. Yu, The physical properties of aqueous solutions of the ionic liquid [BMIM][BF4], J. Solution Chem. 35 (2006) 1337–1346.

[49] W. Liu, L. Cheng, Y. Zhang, H. Wang, M. Yu, The physical properties of aqueous solution of room-temperature ionic liquids based on imidazolium: Database and evaluation, J. Mol. Liq. 140 (2008) 68–72.

[50] S. Paul, A.K. Panda, Physicochemical investigations on the aqueous solution of an ionic liquid, 1-butyl-3-methylimidazolium methanesulfonate, [BMIM][MS], in a concentrated and dilute regime, Colloids Surfaces A Physicochem. Eng. Asp. 404 (2012) 1–11.

[51] A. George, A. Brandt, K. Tran, S.M.S.N.S. Zahari, D. Klein-Marcuschamer, N. Sun, N. Sathitsuksanoh, J. Shi, V. Stavila, R. Parthasarathi, S. Singh, B.M. Holmes, T. Welton, B.A. Simmons, J.P. Hallett, Design of low-cost ionic liquids for lignocellulosic biomass pretreatment, Green Chem. 17 (2015) 1728–1734.

[52] L. Chen, M. Sharifzadeh, N. Mac Dowell, T. Welton, N. Shah, J.P. Hallett, Inexpensive ionic liquids: [HSO4] − -based solvent production at bulk scale, Green Chem. 16 (2014) 3098–3106.

[53] M.E. Hyde, C.E. Banks, R.G. Compton, Anodic stripping voltammetry: An AFM study of some problems and limitations, Electroanalysis. 16 (2004) 345–354.

[54] B. Scharifker, G. Hills, Theoretical and experimental studies of multiple nucleation, Electrochim. Acta. 28 (1983) 879–889.

[55] Y. Yu, L. Sun, H. Ge, G. Wei, L. Jiang, Study on electrochemistry and nucleation process of nickel electrodeposition, Int. J. Electrochem. Sci. 12 (2017) 485–495.

[56] P. Altimari, F. Pagnanelli, Electrochemical nucleation and three-dimensional growth under mixed kinetic-diffusion control: Analytical approximation of the current transient, Electrochim. Acta. 205 (2016) 113–117.

[57] V.A. Isaev, O. V. Grishenkova, Y.P. Zaykov, On the theory of 3D multiple nucleation with kinetic controlled growth, J. Electroanal. Chem. 818 (2018) 265–269.

[58] S. Cherevko, X. Xing, C.H. Chung, Hydrogen template assisted electrodeposition of sub-micrometer wires composing honeycomb-like porous Pb films, Appl. Surf. Sci. 257 (2011) 8054–8061.

[59] H. Ooka, A. Yamaguchi, T. Takashima, K. Hashimoto, R. Nakamura, Efficiency of Oxygen Evolution on Iridium Oxide Determined from the pH Dependence of Charge Accumulation, J. Phys. Chem. C. 121 (2017) 17873–17881.

[60] F.E. Bedoya Lora, A. Hankin, G.H. Kelsall, En route to a unified model for photo-electrochemical reactor optimization. I - Photocurrent and H2 yield predictions, J. Mater. Chem. A. (2017) 22683–22696.

[61] E.M. Siedlecka, W. Mrozik, Z. Kaczyński, P. Stepnowski, Degradation of 1-butyl-3-methylimidazolium chloride ionic liquid in a Fenton-like system, J. Hazard. Mater. 154 (2008) 893–900.