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Redox fusion of metal particles using deep eutectic solvents

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Alternating anodic and cathodic current pulses have been applied to a metal powder on an electrode surface to fuse the particles together. It is shown that homogeneous films can be electroformed with different morphologies depending on the size of the powder and the experimental conditions.

Electroforming is a method to produce complex shaped metallic objects without casting and it involves reducing metal ions in solution around a former primarily using electrodeposition. While this is commonly used, it is slow and coverage may be uneven if the throwing power of the solution is poor. Electroforming is generally carried out in aqueous solutions which limits the metals which can be electroformed due to plating efficiency. It tends to be carried out using metals such as nickel, copper and silver.[1] This study aims to demonstrate that pulsed dissolution and deposition sequences can be used to fuse metal particles together to rapidly form a coating. The process of electrochemically fusing powders together will be referred to here as powder pulse plating (PPP).

Ionic liquids and deep eutectic solvents are of interest in metal deposition for their ability to deposit a wide range of metals in a variety of morphologies.[2] In this investigation deep eutectic solvents (DESs) will be used which are mixtures of quaternary ammonium salts and hydrogen bond donors.[3,4] Ionic liquids and DESs generally have wider potential windows than aqueous solutions and therefore electrodeposition can be carried out with higher current efficiencies.[5] Ionic liquids have been used in a wide variety of other applications[6] including energy storage and conversion for which deposit morphology is important.[7]

Single particle fusion: the first aim of this study was to determine whether the methodology was suitable for fusing a single metal particle to a metal substrate and once this was ascertained, the current pulse parameters required for fusion would be optimised. This study focused on the DES, 1 choline chloride (ChCl): 2 ethylene glycol (EG) and uses zinc powder for the deposition experiments. Conventional zinc electrodeposition has been extensively studied in this DES.[8-10]

Fig. 1a shows a schematic diagram of the concept of PPP. The technique requires sufficient metal to dissolve from the powder under anodic polarisation and time for it to diffuse from the powder to the interface with the substrate before it is deposited under cathodic polarisation. Fig. 1b shows a schematic diagram of the experimental set up (more details are given in the supplementary information). Fig. 1c shows the cyclic voltammogram for the dissolution and redeposition of zinc from a single 600 µm diameter zinc particle and the response is like that shown previously for the bulk deposition and dissolution of zinc from $ZnCl_2$ in the same DES.[11] This shows that the Zn particle remained in contact with the electrode during the experiment. The two anodic stripping potentials at c.a. Ep_1 = -0.8 V and Ep_2 = -0.6 V were the same observed using atomic force microscopy (AFM),[12] and Ep_1 was assigned to the removal of the small scale, nanodeposits whereas the anodic peak, Ep_2, was due to the dissolution of bulk zinc. The oxidation and reduction charges were 23.5 µC and 23.8 µC, respectively, which shows that the process is largely reversible. At slow scan rates, on the anodic cycle, a white cloud was formed around the zinc particle. This is thought to result from either exceeding the solubility of zinc chloride in the double layer or due to the formation of an insoluble zinc glycolate complex which has been seen previously.[13] This means that the length of the anodic pulse will be critical.

Pulse plating is a technique commonly employed for the electrodeposition of many metals from aqueous solutions.[14] In this process metal ions from solution are deposited in a short cathodic potential or current pulse which is then modulated to open circuit or a positive potential/current. This can either enable the diffusion layer to be replenished or dissolve surface irregularities ensuring a smoother surface finish. The suggested optimum higher and lower frequency ranges for pulse plating in aqueous solutions range from 500 Hz to 50 Hz,[15,16] i.e.

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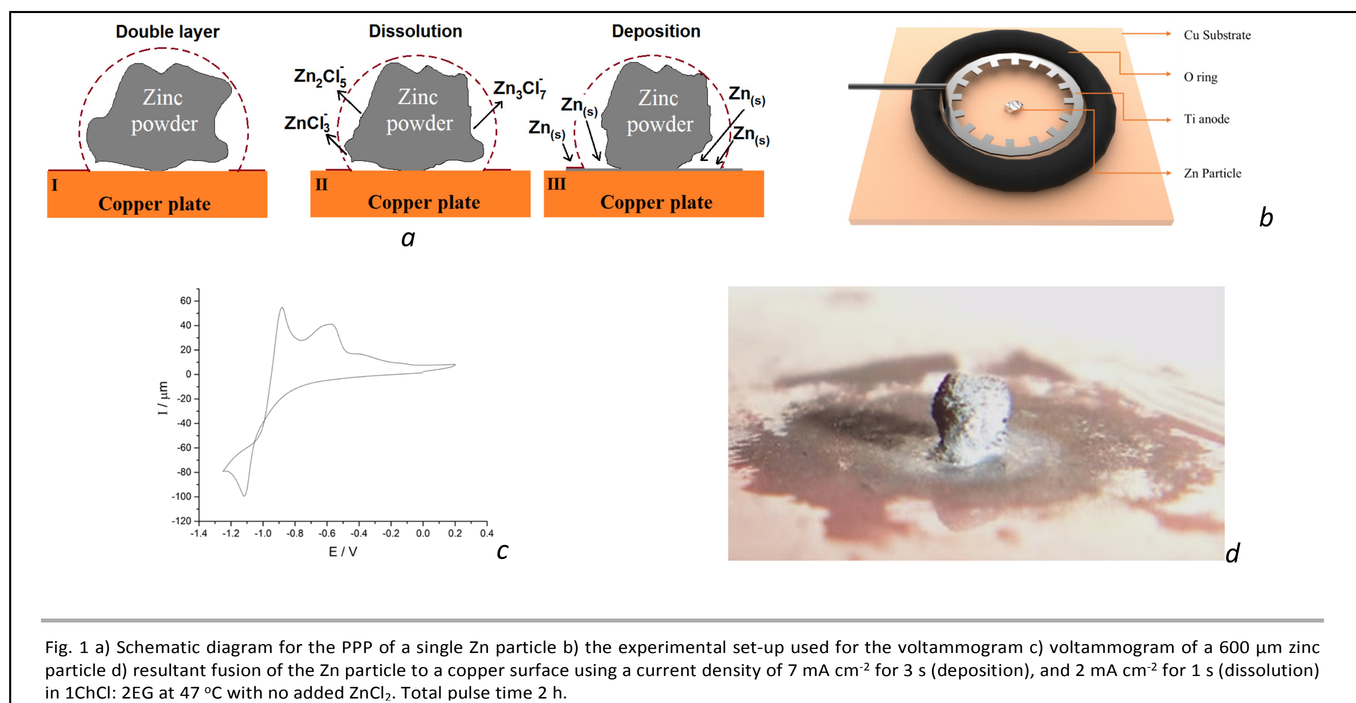

Fig. 1 a) Schematic diagram for the PPP of a single Zn particle b) the experimental set-up used for the voltammogram c) voltammogram of a 600 µm zinc particle d) resultant fusion of the Zn particle to a copper surface using a current density of 7 mA cm^{-2} for 3 s (deposition), and 2 mA cm^{-2} for 1 s (dissolution) in 1ChCl: 2EG at 47 °C with no added $ZnCl_2$. Total pulse time 2 h.

deposition/dissolution/relaxation time periods are in the order of milliseconds. In the current experiment a variety of current pulse periods were performed ranging from 1 ms to 1500 ms and all failed to enable fusion of the 600 µm diameter zinc particle to the surface. It was only when the deposition pulse was between 3 and 6 s (0.33 to 0.17 Hz) and the dissolution pulse was between 1 and 3 s that fusion of the zinc particle to the substrate was achieved. Fig. 1d shows the fusion of a zinc particle to a copper substrate using applied anodic current pulses of 10 mA for 1s followed by cathodic pulses of 35 mA for 3 s. The total deposition time was 3 h. Fig. 1d shows that a layer of fused material approximately 10% of the height of the particle was required to fuse it to the surface. The length of the optimal anodic and cathodic pulse times are relatively logical when the practicalities are considered; the Zn^{II} species will need to travel up to 100 µm to build up a layer close to the electrode. Given that the diffusion coefficient of transition metal ion species in these liquids is approximately 2.47 x 10^{-7} cm^2 s^{-1} then it will diffuse approximately 10 µm in 1 s. So, pulses of less than 1 s will result in transport of insufficient metal to the substrate-solution interface to enable fusion. Fig. 1d shows that a thin halo of zinc is deposited on the copper around the zinc particle. It is clear the during the experiment the zinc ions are unable to diffuse more than 1-2 mm which shows that when other zinc particles are packed together in a layer mass transport will be very difficult.

Dissolution times > 5 s lead to the solution around the particle exceeding the saturation concentration of the Zn^{II} species and this leads to a decrease in the current efficiency of the deposition process.[17]

To determine the length of time required for the Zn particle to fuse to the substrate the experiment shown in Fig. 1 was repeated using 80 - 150 µm diameter Zn particles on a gold coated quartz crystal microbalance. When the particles become attached to the surface they should move synchronously with the substrate and a step change in the mass should occur. It was found 10-12 min were required before a step change in the mass was observed. While fusion occurs after this time, considerably longer time was required to be able to fuse the particles securely to the surface. It also follows that the larger the particles the more metal, and hence the longer the pulse sequence, that is required.

Horizontal electroplating: the strategy to achieve powder pulse plating is to adhere multiple layers of metal powder to a substrate and apply current pulses such that the powder is oxidised and the metal ions in solution are then reduced. For a homogeneous layer to form the fusion must occur between the substrate and the particles and between the particles themselves. It could be argued that pulsing the current, as above, is an inefficient method of electroforming as metal is lost from the surface during oxidation and charge is required for dissolution and deposition. It would be more logical to electroplate around the particles using a solution containing a Zn^{II} species in the same way that composite materials are deposited.[18] The difference, however, is that metallic particles are conducting so the electrified interface extends to that between the particles and the solution rather than at the substrate-solution interface. A direct current of 48 mA was applied for 2 h to a 3 x 3 cm copper substrate which was covered with 80 - 150 µm diameter Zn particles in a 1 ChCl: 2 EG DES containing 0.3 mol dm^{-3} $ZnCl_2$ dissolved in at 47 ± 2.5 °C. Although a grey, metallic deposit was obtained, it lifted from the substrate and immediately crumbled. The reason for this is shown schematically in Fig. 2a. Fusion occurs preferentially at the powder-solution interface rather than the substrate-powder interface as this is where Zn^{II} diffusion is higher.

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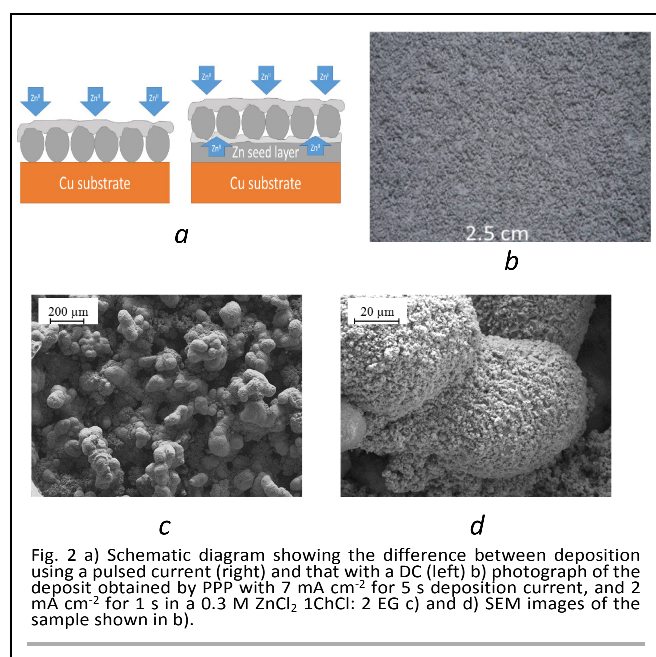

Fig. 2 a) Schematic diagram showing the difference between deposition using a pulsed current (right) and that with a DC (left) b) photograph of the deposit obtained by PPP with 7 mA cm^{-2} for 5 s deposition current, and 2 mA cm^{-2} for 1 s in a 0.3 M $ZnCl_2$ 1ChCl: 2 EG c) and d) SEM images of the sample shown in b).

To obtain fusion between the zinc powder and the substrate it is necessary to use alternating current pulses. Initial experiments using 7 mA cm^{-2} for 5 s (deposition) and 2 mA cm^{-2} for 1 s (dissolution) caused the Zn particles to fuse well at the solution interface but adhesion to the substrate was poor. It was thought that this is due to a low Zn content under the powder layer at the interface with the substrate. To circumvent this, it would be better to have a seed layer of Zn at the substrate-powder interface. Before starting each experiment, the copper substrate was cathodically polarised for 10 min in a 0.3 M $ZnCl_2$ 1ChCl: 2 EG at a DC current density of 50 mA cm^{-2} to create a seed layer of zinc (approximately 1-2 µm thick) to act as a zinc reservoir to keep the zinc concentration high close to the bottom of the close packed zinc layer. The copper plate working electrode was spring loaded to ensure a constant pressure with the edges of the holder (see supplementary information for further details).

Several methods of loading the zinc particles on the substrate surface were attempted. The most important parameter appeared to be the size of the particles. Below 50 µm, the colloidal dispersions were too stable, and the particles did not settle well onto the substrate surface. This led to fusion, but the low packing density meant that the particles showed poor adhesion to the surface and to each other. To overcome this issue, larger zinc particles sized between 80-150 µm were used. After the copper substrate was coated with a thin layer of zinc, the zinc powder was stirred into the DES for 10 s and left to settle onto the substrate for 2 min before a series of current pulses were applied in an unstirred system. The current pulses were 7 mA cm^{-2} for 5 s (deposition) and 2 mA cm^{-2} for 1 s (dissolution). Current densities were calculated for the size of the substrate rather than the surface area of the particles. The experimental procedure is described in more detail and shown schematically in the supplementary information (Fig. S3). Fig. 2b and c show SEM images of the Zn film formed under different magnifications. At high magnification the usually smooth particles can be seen to be decorated on the surface. Under lower magnification the top surface is relatively loosely packed although the lower layers appear denser. The deposit was approximately 0.18 mm thick which is considerably thicker than could be electrodeposited using conventional DC electroplating using similar conditions (typically 6-10 µm, see below). This shows that PPP is an alternative way of producing electroformed material on a conducting substrate. It should however be noted that thicker layers can be produced in a similar timescale by layering more Zn powder on the electrode surface.

Vertical electroplating: in the previous experiment the high viscosity and ionic charge of DESs was seen as an issue as it stabilised colloidal dispersions, as observed previously,[19] and prevented the powder settling on the substrate. Electroforming is conventionally used for complex geometries and so limiting it to a horizontally oriented flat substrate is not particularly useful. A different approach was used which was similar with those used in aqueous solutions to produce composite materials. In this case, fine zinc particles (6 to 9 µm in diameter) were distributed in a DES and zinc was plated from a 1ChCl: 2EG DES containing 0.3 mol dm^{-3} $ZnCl_2$. The cathode was placed vertically, and a pulsed current was applied.

As previously, the copper substrate was cathodically polarised for 10 minutes in 65 ml of 0.3 M $ZnCl_2$ in 1ChCl: 2 EG at a DC current density of 50 mA cm^{-2}. Following the deposition of an initial 1-2 µm thick zinc layer 0.05 g of Zn particles were then added to the DES. A cathodic pulse of 6.1 mA cm^{-2} was applied for 5 s and an anodic pulse of 2 mA cm^{-2} was used for 1 s with a total plating time 3 h. The main difference with the horizontally oriented samples, listed above, was that the solution was periodically stirred (10 s ON and 5 min OFF) to ensure the zinc particles stayed in solution but also had time to fuse with the substrate. The stirrer was connected to a programmable Arduino-UNO logic board to control the stirring pulses. The total coating time was 180 min. The deposit obtained (Fig. 3) was significantly different from those observed in Fig. 2; the zinc coating is denser, and each Zn particle has become coated in small, well defined zinc crystallites. Hexagonal single crystals can be seen and XRD analysis shows that the 101 and 100 crystal faces dominate. This behaviour has previously been observed for the electrodeposition of Zn from this DES.[11]

Fig. 3d shows a cross section of the sample shown in Fig. 3a and it can be seen that packing density is quite high but there are some macroscopic holes in the sample. Because the Zn particle are quite small it could be questioned whether they are incorporated at all but repeating the experiment using a DC deposition experiment with the same current density without the Zn particles led to a much thinner coating, a cross section of which is shown in Fig. 3e. It can be seen that the suspended particles gives a film which is approximately 6 times thicker when particles are suspended in the solution.

Current Efficiency: since some of the zinc incorporated into the deposit is from the particles and has not been electrochemically reduced, the mass obtained could potentially be higher than that from a 100% efficient Faradaic deposition process. The mass deposited in the experiments above was determined

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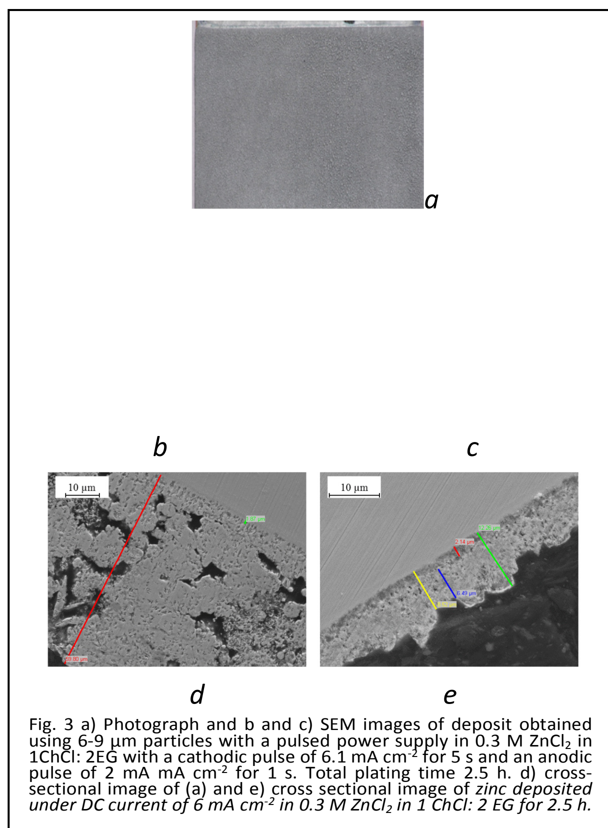

Fig. 3 a) Photograph and b and c) SEM images of deposit obtained using 6-9 µm particles with a pulsed power supply in 0.3 M $ZnCl_2$ in 1ChCl: 2EG with a cathodic pulse of 6.1 mA cm^{-2} for 5 s and an anodic pulse of 2 mA mA cm^{-2} for 1 s. Total plating time 2.5 h. d) cross-sectional image of (a) and e) cross sectional image of *zinc deposited under DC current of 6 mA cm^{-2} in 0.3 M $ZnCl_2$ in 1 ChCl: 2 EG for 2.5 h.*

gravimetrically using a 5 dp balance and compared with that which would be expected from Faraday's law. The sample obtained from PPP in the horizontal orientation yielded 1.65 times more mass than would be expected from the charge passed whereas that in the horizontal orientation was almost that predicted by Faraday's law (0.96). The conventional electroplated sample was only 87% current efficient.

An additional issue that has been observed with the deposition of metals from DESs is that the deposition of very thick coatings is often difficult by DC deposition. Once the deposit is > 20 µm the morphology changes and black friable deposit is often obtained. Powder pulse plating allows thick deposits to be obtained comparatively quickly albeit with a porous structure. To see whether these efficiencies are reasonable, it is possible to calculate an ideal super efficiency by considering what the efficiency would be by packing a spherical particle together into a lattice. For a sphere, the packing efficiency in a cubic lattice is approximately 52% ($(4\pi r^3/3)/(8r^3)$). Using a DC supply to deposit 48 g of Zn would trap a maximum of 52 g of Zn particles so the maximum current efficiency would be 208% (100/48). Given that the packing of the zinc particles is relatively dispersed a deposition efficiency of 165% is quite respectable.

In conclusion, this study has shown that zinc particles can be attached onto a substrate through alternating anodic and cathodic charge cycles. It was found that when the substrate was held in a horizontal orientation large zinc particles needed to be used to ensure the particles retained a good physical contact with the substrate. Cycling the current under these conditions enabled homogeneous zinc layers to be deposited. The anodic cycle was clearly levelling the large zinc particles.

To enable zinc plating in the vertical orientation small zinc particles were suspended in the electrolyte. Under these conditions, thick, homogeneous deposits were obtained demonstrating that powder pulse plating is a viable method for coating a surface. It was found that under some conditions, super-efficient deposition could be obtained. This clearly occurs due to zinc being incorporated onto the surface which did not need to be electrochemically reduced. Efficiencies of up to 165% with average of 140% were recorded. This is quite high given the packing density of the zinc particles.

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Conflicts of interest

The authors report no conflicts of interest

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