Surface Pb Nanoparticle Aggregation, Coalescence and Differential Capacitance in a Deep Eutectic Solvent Using a Simultaneous Sample-Rotated Small Angle X-ray Scattering and Electrochemical Methods Approach

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Abstract

Nanoparticle electrodeposition is a simple and scalable approach to synthesizing supported nanoparticles. Used with a deep eutectic solvent (DES), surface nanoparticles can be assembled and exhibit unique surface charge separation when the DES is adsorbed on the nanoparticle surface. Key to understanding and controlling the assembly and the capacitance is a thorough understanding of surface particle mobility and charge screening, which requires an *in-situ* approach. In this study, Pb particle formation, size, shape and capacitance are resolved in a 1:2 choline Cl: urea deep eutectic solvent whilst sweeping the cell potential in the range: 0.2 V to -1.2 V (vs. Ag/AgCl). These system parameters were resolved using a complementary suite of sample-rotated small angle X-ray scattering (SR-SAXS) and electrochemical impedance spectroscopy (EIS), which are presented and discussed in detail. This approach is able to show that both particle and ion transport are impeded in the DES, as aggregation occurs over the course of 6 minutes, and dissolved Pb ions accumulate and remain near the surface after a nucleation pulse is applied. The DES-Pb interactions strongly depend on the cell potential as evidenced by the specific differential capacitance of the Pb deposit, which has a maximum value of $2.5 \pm 0.5 \text{ F g}^{-1}$ at -1.0 V vs. Ag/AgCl. Altogether, the SR-SAXS-EIS approach is able to characterize the unique nanoparticle capacitance, mobility and ion mobility in a DES and can be used to study a wide range of nanoparticle deposition systems *in-situ*.

Graphical Abstract

Keywords

nanoparticle, synthesis, electrodeposition, deep eutectic solvent, stability, X-ray scattering, SAXS, USAXS, impedance, electrostatic, capacitance, differential capacitance, aggregation, coalescence, Pb nanoparticles

1. Introduction

Nanoparticle electrodeposition is a simple and cost-effective, bottom-up approach to synthesizing supported nanoparticles[1], which can be used in a variety of nanotechnologies[2]. Owing to its simplicity, electrodeposition is a scalable process that has historically been used in electroplating thin films[1]. Nanoparticle electrodeposition, on the other hand, presents new challenges, particularly pertaining to nanoparticle stability[3], monodispersity[4], and size control[5]. While the latter two concerns can be addressed by tuning the deposition parameters[6-9], the surface particles are mobile[10] and readily aggregate and coalesce[11] into clusters[3, 12]. In general, nanoparticles are stabilized against aggregation by incorporating a stabilizing agent, which adsorbs onto the particle surface to achieve electrostatic, steric or electro-steric mutual repulsion of neighboring particles.[13] This has lead to the pursuit of novel solvents for electrodeposition, which readily adsorb onto particle surfaces as they are synthesized and can dissolve a wide range of metal precursors.

Deep eutectic solvents are a class of tunable, cost-effective and environmentally friendly solutions that are being used in a wide range of electrochemical applications[14]. DESs typically consist of a quaternary ammonium salt and a hydrogen bond donor, at their eutectic composition, and can dissolve a wide range of metal precursors.[15] Mixed together, these two (otherwise solid) components form a clear liquid at room temperature and have been extensively employed since their discovery in 2001.[16] Owing to their unique interactions and propensity to adsorb onto particle surfaces, DESs can both stabilize and assemble nanoparticles during synthesis[17-22]. Therefore, the particle-DES interactions and particle mobility must be understood and are the focus of this study.

1.1 Particle-DES Interactions

As the constituent species of a DES are typically too small to achieve steric stabilization, electrostatic stabilization is considered here as the primary stabilization mechanism. This is a process whereby the surface is charged via: ionization of surface groups, ion adsorption, dissolution of ionic solids or isomorphous substitution.[23] Regardless of how the surface is charged, the excess charge must be screened by counter ions. This process results in a local capacitor and an electrostatic surface potential that repels other particles.[23] Both of these

consequences are desirable for application as electrochemical supercapacitors (EC)[24] and in a broad range of nanotechnologies[2].

The surface charge screening in DESs is in many ways different from that occurring in traditional aqueous solutions or in room temperature ionic liquids.[25-28] While DESs have been effective in producing electrochemical super-capacitors[29-32], the spatial distribution of charge differs significantly from aqueous solution. For example, charged separated perturbation layers have been observed at the nanoparticle surface and extend several nanometers from the surface.[20, 25] While this phenomena is likely due to the adsorption of the DES, it is unclear which DES-nanoparticle systems would exhibit this behavior. With the large number of possible combinations and the limited accessibility of synchrotron radiation, the differential capacitance can provide some insight into the interactions between the nanoparticles and DES. For this reason, the differential capacitance was obtained with the X-ray scattering data presented in this study.

Experimentally, the differential capacitances of only a small fraction of DESs have been evaluated. The differential capacitances of these DESs are markedly different from aqueous solutions and depend on both the hydrogen bond donor, as well as the electrode surface.[27, 28] With this study, we will show how the specific differential capacitance in a 1:2 choline Cl:urea DES exhibits marked variations on the surface of suspended Pb nanoparticles. Used in combination with the small angle X-ray scattering (SAXS), the specific capacitance can be obtained when multiple cathodic reactions are present, which prevent a mass determination from the faradaic current. This completely *in-situ* approach is presented and discussed in this paper.

1.2 Surface Small Angle Scattering

While all electrochemical investigative techniques are performed in solution, other techniques that probe the physical dimensions of surface phases are often difficult to incorporate *in-situ*. X-rays, on the other hand, readily penetrate the solution and can be used *in-situ*. Specifically, SAXS provides an experimenter with the opportunity to resolve nano-scale phases *in-situ* and over much larger electrode areas compared with modern microscopes. However, SAXS is not as common as electron microscopes, as it not as accessible and can often times be ambiguous. In this paper, the combined sample-rotated

SAXS /EIS approach is presented and was developed specifically to address data ambiguity.

The overall goal of this technique is to provide a comprehensive characterization of the surface and provide the experimenter with better model certainty.

Data ambiguity in small angle scattering (SAS) often arises when the scattering phases are unknown. The combined SR-SAXS/EIS approach reduces this ambiguity by: 1) probing the scattered intensity in three dimensions, 2) providing absolute scattering length densities and volume fractions of scattering phases and 3) correlating the physical dimensions of surface phases with the electrochemical response. In a typical Grazing Transmission SAXS (GTSAXS) experiment, the scattering from surface phases is collected by tilting the sample surface to angles greater than the critical angle.[33] In this way, the dimensions of surface phases, both parallel and perpendicular to the surface, can be extracted from a 2D SAXS image. The difference between a grazing transmission geometry and sample-rotated, used here, is that the incident X-rays are applied to different sample angles that are much larger than the critical angle to avoid the complications of a distorted surface wave. The SR-SAXS approach may be preferred over a grazing incidence (GISAXS) or GTSAXS approach when there is no surface ordering and there are restrictions in cell design. Furthermore, the SR-SAXS can be extended to collect several SAXS patterns at different sample angles, which can remove some model ambiguity when the scattering is anisotropic.[25] In this article, the *in-situ* geometry, data treatment and analysis are discussed in detail and can be applied to a very broad range of electrochemical systems with uniquely anisotropic surface phases.

1.3 Particle Mobility and Aggregation

Surface particle mobility is usually inferred from a post-mortem analysis of a sample. Very few *in-situ* techniques[10] exist that allow an experimenter to observe the change in surface particle morphology with time. Most often, this is because aggregation occurs on sub-second time scales[3] and it is difficult to probe through the solution. However, synchrotron X-rays can easily penetrate solutions and have been used to observe aggregation and coalescence *in-situ* in a DES where particle mobility is sufficiently slow[25]. The same SR-SAXS approach[33] is used here simultaneously with electrochemical techniques. We note that in the before mentioned article, the GTSAXS terminology was used. These techniques are complementary, since the data from one technique can be used to extract more data from the

other. Specifically, the anodic chronoamperometry data is used to obtain the absolute scattering cross-section from the SR-SAXS data, while the SR-SAXS data is used to obtain the specific differential capacitance of the Pb particles from the electrochemical impedance spectroscopy (EIS) data. Use of the SR-SAXS is necessary, in this study, because additional cathodic reactions occur, which prevent the use of the cathodic faradaic charge passed at each cathodic potential to calculate the deposit mass. Furthermore, the combined SR-SAXS/EIS approach could resolve any morphological dependence on the differential capacitance.

However, this is not observed here.

1.4 Pb Electrodeposition

Lead electrodeposition has been used to study the fundamental deposition mechanism in both aqueous[34] and room temperature ionic liquids[35]. In the field of quantum dot synthesis[36], PbS particles have been studied and assembled using DES and using solution synthesis methods[18]. While PbS thin films have been co-deposited using thiourea[37] (a possible DES component), quantum dots have not. Therefore, the aim of this study is to understand Pb nanoparticle electrodeposition in a DES towards PbS quantum dot synthesis. From an fundamental perspective, Pb was used to: maximize the X-ray contrast in the deposit, to observe any aggregation/coalescence[11] and capacitance change of deposited particles, and to observe how the particle deposit dissolves. Therefore, the *in-situ* evolutions of the deposit morphology (using SR-SAXS) and of its capacitance (using EIS) are characterized in the potential range: 0.2 V to -1.2 V. Since SR-SAXS analysis requires some modifications to a typical small angle scattering (SAS) analysis, a detailed discussion is provided in the Theory section.

2. Experimental

2.1 Materials

The DES solution was prepared by mixing recrystallized choline Cl⁻ (Sigma-Aldrich) and urea (Sigma-Aldrich) in a 1:2 molar ratio in absolute ethanol. The mixture was left to melt on a hot plate at 90°C and under an Ar blanket. Once a homogenous liquid was observed, 0.002 wt.% PbCl₂ (~0.01mM) was added, mixed and stirred under an Ar blanket. The PbCl₂/DES mixture was allowed to dissolve under these conditions for 6 hours to obtain the final, clear solution. This final solution was transferred to a sealed glass container and stored. The

working and counter electrodes used in these experiments were 180 μm thick glassy carbon (HTW) and Pt mesh (Sigma Aldrich), respectively. A leakless Ag/AgCl reference electrode (eDaq) was used in the electrochemical cell. Therefore, all voltages reported here are versus Ag/AgCl.

2.2 X-ray Scattering

Sample rotated small angle X-ray scattering (SR-SAXS) experiments were performed using the custom designed electrochemical cell reported previously and at sample angles of 45° , 30° and 20° . [25] These experiments were performed at the USAXS beamline at sector 9-ID, Advanced Photon Source at an X-ray energy of 18 keV. [38] These data are on an absolute scale when normalized by the sample thickness. Some attenuation was necessary to avoid beam damage in these experiments and was observed by either bubble formation or X-ray induced changes in the open circuit potential. For these experiments, transmissions of 10% were sufficient to avoid this beam damage. All of the SR-SAXS fitting was performed using the Imfit module for python [39], while the normal SAXS model fitting was accomplished using the Irena package for Igor pro [40].

2.3 Electrochemistry

To characterize the Pb-DES system, we report first the cyclic voltammogram of the cell, which was obtained using a scan rate of 50 mV s^{-1} between 0.2 V and -1.3 V, as this is the electrochemical window for the DES at room temperature and without a metal salt. [20] These data are used to qualitatively characterize the electrochemical system. The main focus of this paper is the potential sweep procedure, which employed: chronoamperometry, electrochemical impedance spectroscopy (EIS) and SR-SAXS. In this procedure, the cell was polarized between 0.2 V and -1.2 V at 0.1 V to 0.2 V increments. In regions where Pb is present on the surface, potential steps of 0.1 V were used, which corresponds to the potential range: -0.8 V to -1.2 V and back to -0.6 V. A step of 0.1 V was chosen because it was small enough to capture significant changes in the EIS and large enough to make the best use of beam time. Steps of either 0.1 V or 0.2 V were used outside this range for time constraints, as the EIS did not change significantly. The SR-SAXS/EIS procedure, at each step, is explained in the following section (2.4). Electrodeposition experiments in the main article were performed only after complete dissolution of the substrate. In each case, the potential was

held at the electrodeposition potential during data collection. Short electrodeposition pulses were not possible and discussed in the Supplementary Section A.2.2.

All of the electrochemical measurements were obtained using a Gamry Reference-600 potentiostat. At each potential, Φ , the cell capacitance was obtained from the potentiostatic electrochemical impedance spectroscopy (EIS) using the Gamry frameworks software. These impedance measurements applied a single sinusoidal single of 10 mV (root-mean-squared) above the DC offset at each potential, Φ , and at a range of frequencies. The frequency range between 0.1 Hz $< f < 10000$ Hz was evaluated, with 10 log-spaced frequencies per decade.

2.4 SR-SAXS/EIS Procedure

Key to this approach is the electrochemical and X-ray scattering data collection at each potential step where the cell was polarized to a specified potential, Φ (in V vs. Ag/AgCl). The time sequence of the EIS and SR-SAXS are shown for one potential (-0.9 V) in Figure 1. At each step, the cell was polarized for 10 s to allow the system to reach a steady state current. Ideally, the EIS and SR-SAXS should be collected simultaneously. However, rotation of the cell while collecting EIS data can result in unwanted noise. Therefore, the SR-SAXS data collection was started in the middle of the EIS such that the first 45° SAXS data was finished at the same time. Following the EIS, the cell was held at the potential, Φ , for 17 minutes to allow the rest of the SR-SAXS to finish. Typically, the SR-SAXS was finished ~ 10 minutes to 13 minutes before 17 minute polarization completed; this extra time allowed for some growth between SR-SAXS collection, as well as any necessary (USAXS) instrument tuning. Once the 17 minute polarization completed, the cell was polarized to the next Φ value and the procedure repeated. Therefore, the procedure can be summarized as a chronological sequence of: chronoamperometry, EIS, chronoamperometry, with some dead time in-between steps.

3. Theory

3.1 SR-SAXS

In a typical small angle scattering experiment, the scattered intensity is measured as a function of the scattering vector, $\mathbf{q}$. The shape of $I(\mathbf{q})$ is then used to obtain the size and shape of the scattering phases. In the case where the scattering phases are anisotropic and confined to a surface, a grazing transmission geometry has been shown to be a powerful approach to resolving their size and shape by collecting X-ray scattering data at different sample

orientations.[25] Here, the sample angles were chosen to maximize the scattering signal and small angle scattering was collected at lower q to resolve larger phases. In all of the SR-SAXS data, the absolute intensity was obtained by initially assuming a sample thickness, T_s , of 1 mm; this is a necessary correction in the data reduction software. As the Pb deposit is confined to the surface, the mean height of the particles, $\bar{H}$, is obtained from the model fitting and used to obtain the absolute scattering cross-section[41]. During nucleation, $\bar{H}$ could not be extracted from a model fit and therefore the intensity units are arbitrary (a.u.). The absolute intensity of any small angle scattering data scales with the square of the total volume and contrast of the scattering population.[42] This means that without knowledge of one, it is difficult to know the quantity of the other (within a useful margin). For an electrochemist, a convenient solution to this problem is to combine the electrochemical data with the small angle scattering (SAS) data. This procedure is unfortunately not common and therefore deserves some introduction.

By combining the faradaic charge from the chronoamperometry data with the density of the deposit, one could calculate the total volume. The only requirements are that the faradaic reactions are known and quantifiable and the density of the deposit is known. In this case, the deposit volume can be taken directly from the anodic current and put into the SAS model. However, in this study and in many real systems, there are side reactions (O_2 reduction) that prevent the faradaic cathodic charge from being used to calculate the total volume. The O_2 reduction is irreversible in the potential window evaluated here and will be discussed in Section 4.1. Therefore, the anodic charge contains only Pb dissolution at -0.6 V and is used to calculate the total particle volume. With the total particle volume and scattering length density known, the scattering length density of the surrounding solution can be calculated and compared with expected theoretical values. Furthermore, if one can assume this stays approximately constant, the volume (and therefore mass) of the particles at each potential can be calculated and used with EIS measurements to obtain the specific differential capacitance. In this manner, the chronoamperometry data is used to extract more information from the SR-SAXS, which can then be combined with EIS data.

3.1.1 Nucleation/Growth/Aggregation (-0.8 V)

On the initial cathodic sweep, SAXS was first observed at -0.8 V. Unlike subsequent data, the

morphology of the Pb deposit evolves over time and cannot be fit to a single model. For this reason, no shape determination of the deposit morphology at -0.8 V can be made and the scattering data are referred to as SAXS data, as each curve was fit separately. For this reason, only the evolution in particle structure can be extracted during this time and nothing conclusive can be reported about the shape of the particles. In these data, the slit-smeared SAXS could have some anisotropy but cannot be resolved. Therefore, the model smearing was performed by assuming particle isotropic scattering. Consequently, only the radius of gyration, R_g , of the particles and any hierarchical structure can be reliably reported. For aggregated particles, their structure is related to their fractal dimension, d_m . [43] The unified approximation is ideal for modeling such systems since it combines the robust Guinier and Porod relationships with the power-law scattering one expects from a fractal-like aggregates. [44, 45]

After 2 minutes, the first SAXS data (45°), revealed only very weak scattering that cannot be reliably modeled. The following scan (30°), collected 4 minutes after, revealed a clear Guinier knee and was modeled using a single-level unified equation:

$$1. \quad I_p(q) = G_p e^{\frac{-q^2 R_g^2}{3}} + B_p \left[\frac{\left(\operatorname{erf} \left(\frac{q R_g}{\sqrt{6}} \right) \right)^3}{q} \right]^4 + bckg$$

$$2. \quad B_p = \frac{2\pi G_s A_p}{V_p^2}$$

where G_p is proportional to the volume squared and contrast squared of the primary particles, R_g is the radius of gyration of the primary particles, A_p and V_p are the surface area and volume of spheres having a radius equal to $R_g \sqrt{5/3}$ and $bckg$ is a constant representing the background scattering. To ensure the feasibility of the model, B_p is calculated from G_p (Equation 2) and assumes the particles have a surface to volume ratio of a sphere. From the model fit of Equation 1, an R_g of $58 \text{ nm} \pm 3 \text{ nm}$ was found for the SAXS data obtain 4 minutes after the nucleation.

Six minutes after nucleation, the SAXS data revealed a power-law decay in intensity that preceded the Guinier knee. Therefore, the data were fit the two-level unified equation:

$$3. \quad I_A(q) = B_A e^{\left(\frac{-q^2 R_g^2}{3}\right)} [q]^{d_m} + I_p(q)$$

where d_m is the mass fractal dimension and B_A is a scaling constant. From the model fitting of Equation 3 to the SAXS data an R_g of $62 \text{ nm} \pm 4 \text{ nm}$ and d_m of 2.5 ± 0.5 were found. The difference between Equations 1 and 3 is the lack of particle structure in the former (4 minutes). Therefore, from the fits of Equations 1 and 3 the size and structure of the particle deposit before and after aggregation are obtained, respectively.

3.1.2 Particle Growth

Unlike ordinary slit-smeared SAXS, the slit-smeared SR-SAXS can resolve surface anisotropy. In the potential range: -0.9 V to -1.2 V and -1.2 V to -0.7 V, all three of the SR-SAXS data (45° , 30° and 20°), collected at each potential, are fit to a system of oriented ellipsoids that are polydisperse in size. From each model fit, the time-averaged physical dimensions and volume fraction of the Pb deposit over the course of 6 minutes are obtained. Therefore, this analysis is limited to systems with nucleation and growth kinetics that are sufficiently slow. In cases where sufficient particle nucleation is present, one can expect to see a broadening of the size distribution as smaller particles are deposited. On the other hand, if significant growth occurs over the scan period, the faradaic current should be incorporated in the model fit to obtain the particle size and shape accurately. Such a formulation is discussed later in Section 4.2.2.a where particle growth is included in the model fitting. In the potential range: -0.9 V to -1.2 V and -1.2 V to -0.7 V, both nucleation and growth are minor effects in these experiments. However, it is important for an experimenter to consider these effects and therefore they will be discussed further in Section 4.

The scattered intensity from an oriented spheroid, is the same as that of a perfect sphere with an effective radius, R_{eff} . [42] The value of R_{eff} is calculated using the scattering vector, $\mathbf{q}_R$, radius, R , and aspect ratio, AR by the equation:

$$4. \quad R_{eff}(\mathbf{q}_R, R) = \sqrt{R^2 \left(\frac{q_x}{|\mathbf{q}_R|}\right)^2 + R^2 \left(\frac{q_y}{|\mathbf{q}_R|}\right)^2 + R^2 AR^2 \left(\frac{q_z}{|\mathbf{q}_R|}\right)^2}$$

where the x , y , z directions and $\mathbf{q}$ vectors are shown in Figure 1, where the $\mathbf{q}$ vectors are

oriented rather than the sample for simplicity.[42] For the slit-smeared geometry used in these experiments, the scattered intensity, I , was collected as a function of the scattering angle perpendicular to the surface, $\theta_{\perp}$. The intensity, I , at each $\theta_{\perp}$ was slit-smeared with the scattered intensity parallel to the glassy carbon surface, which is a function of the parallel scattering angle, $\theta_{\parallel}$. With the sample angle, α , as well as $\theta_{\perp}$ and $\theta_{\parallel}$, obtained from the instrument geometry, the scattering vector $\mathbf{q}_R$ is calculated by the Equations:

$$\begin{aligned} 5. \quad & \mathbf{q}_R(q_{\parallel}, q_{\perp}, \alpha) = q_x i + q_y j + q_z k \\ 6. \quad & q_x = \frac{2\pi(\cos(-\alpha - \theta_{\perp}) \cos \theta_{\parallel} - \cos \alpha)}{\lambda} \\ 7. \quad & q_y = \frac{2\pi(\sin \theta_{\parallel})}{\lambda} \\ 8. \quad & q_z = \frac{2\pi(\sin(-\alpha - \theta_{\perp}) \cos \theta_{\parallel} - \sin \alpha)}{\lambda} \end{aligned}$$

With the values of $\mathbf{q}_R$ and the slit-length, q_{slit} , known, the scattered intensity from a size distribution of particles can be calculated. The slit-smeared scattered intensity from a Gaussian distribution, $P(R)$, of oriented ellipsoid is then:

$$\begin{aligned} 9. \quad & I_{smr}(q_{\perp}, \alpha) = \frac{K}{\sin \alpha} \int_0^{q_{slit}} I(\mathbf{q}_R(q_{\parallel}, q_{\perp}, \alpha)) dq_{\parallel} \\ 10. \quad & I(\mathbf{q}_R(q_{\parallel}, q_{\perp}, \alpha)) = \int_{0.01R}^{100R} V_p F^2(\mathbf{q}_R, R) P(R) dR \\ 11. \quad & F(\mathbf{q}_R, R) = \left[\frac{3 \left[\sin(|\mathbf{q}_R| R_{eff}(\mathbf{q}_R, R)) - |\mathbf{q}_R| R_{eff}(\mathbf{q}_R, R) \cos|\mathbf{q}_R| R_{eff}(\mathbf{q}_R, R) \right]}{[|\mathbf{q}_R| R_{eff}(\mathbf{q}_R, R)]^3} \right] \end{aligned}$$

where the subscripts $\parallel$ and $\perp$ are directions of the scattering vector, parallel to the surface and perpendicular to the surface, respectively, α is the sample angle, q and $\mathbf{q}$ are the reciprocal space magnitude and vector, respectively, K is a scaling constant (cm^{-4}), R is the radius of the spheroid, AR is the aspect ratio, V_p is its volume and $P(R)$ is a gaussian function that scales the scattering from particles of size R , using the standard deviation, σ , and mean particle radius, $\bar{R}$. [42, 46]; the units of $P(R)$ are nm^{-1} . The scaling constant, K , is proportional to the total particle volume per irradiated volume (i.e. volume fraction), ν , and X-ray contrast, $\Delta\rho$. These values can be extracted from K when one is known. From the model fit of Equation 9 to the SR-SAXS data, the values of: K , AR , $\bar{R}$ and σ are extracted

as a function of potential. It is important to note that Equation 9 is two dimensional in reciprocal space. This allows the scattered intensity obtained at different sample angles, α , to be fit to a single equation.

3.2 Electrochemical Impedance Spectroscopy (EIS)

The EIS data were fit to an equivalent circuit that contains the solution resistance, R_s , in series with a parallel circuit that represents the surface charge transfer resistance, R_t , and capacitance, which is taken to be a constant phase element, CPE. The equivalent circuit was fit to these EIS data in the frequency range of $0.1 \text{ Hz} < f < 10000 \text{ Hz}$ and given by the equation:

12.

$$Z(\omega) = R_s + \left(1/R_t + (\omega\sqrt{-1})^\gamma Q\right)^{-1}$$

where ω is the angular frequency, Q has units of $s^\gamma \Omega^{-1}$ and γ is an exponent that approaches one for a narrow distribution of resistances, R_t . [47] In Equation 12, the value of R_t represents the charge transfer resistance at the surface, while Q is related to the total surface charge. In Equation 12, a constant phase element (CPE) is used instead of a capacitor to account for a distribution in R_t , since the value of γ was always greater than 0.9. [48] In some cases, the EIS model fits could be improved by accounting electroactive adsorption, as reported previously. [25] These EIS data were obtained immediately following nucleation and growth (-0.9 V) and the onset of dissolution (-0.7 V). However, only minor improvements to the model fit were obtained with relatively large errors associated with the fit parameters. These model fits can be found in the Supplementary Section A.1.

4. Results and Discussion

4.1 Cyclic Voltammetry

The Pb-DES system was characterized by three sequential cyclic voltammograms shown in Figure 1. There are three notable observations: 1) there is one cathodic peak and one anodic peak, 2) there is more cathodic charged passed for each cycle and 3) there is an increase in the peak current with scan number. As the current, I_c , was swept to cathodic potentials less than -0.8 V, the Pb precursor was reduced on the glassy carbon surface. The deposited Pb particles continue to grow on the anodic sweep until $\sim -0.7 \text{ V}$, at which point the Pb deposit oxidizes and is removed from the surface; this is confirmed with SAXS measurements.

Therefore, the Pb-DES system is reversible, which makes it an ideal system to study nucleation, growth and dissolution *in-situ* without changing the sample cell.

In all scans, there is slightly more cathodic charge passed than anodic charge. In the first scan there is 13% more charge passed, while only 6 % more cathodic charge is passed in the final scan. This extra cathodic charge is attributed to the presence of small amounts of oxygen[49] in the solution that was unavoidable in these experiments. The presence of O₂ has two major consequences for the Pb-DES system: 1) it precludes precise deposit mass determination from the cathodic region of Figure 2, as O₂ is reduced[49] at the same time as the Pb precursor and 2) a galvanic couple can form between deposited Pb and O₂, which will dissolve the Pb if the cell is not polarized; this is demonstrated and discussed further in the Supplementary Section A.2. Based on previous work in a 1:2 choline Cl:ethaline DES, an O₂ reduction peak in the CV was observed between -0.63 V and -0.78 V vs. Ag/AgCl[49], which is very near that of Pb oxidation. It was estimated that during the polarization sweep, the Pb current efficiency, η , was ~ 70 % in the cathodic region. This approximation is detailed in the Supplementary Section A.3 and is used to estimate particle growth during the SR-SAXS data set.

The increase in peak current could be attributed to an increase in the diffusion coefficient of the Pb precursor near the glassy carbon, though this was not explored further[50]. However, it will be shown that there is a significant increase in the concentration of the Pb precursor, near the glassy carbon surface, following electrodeposition, which is expected to reduce ion mobility[50].

4.2 SR-SAXS and EIS Results

4.2.1 SAXS

The model fits shown in Figure 3 are unable to extract any shape information from the particle deposit. Based on the SR-SAXS modeling and the fact that these particles are confined to the surface, the particle aggregate could be slightly anisotropic but is difficult to determine from only one SAXS data set. These aggregates coalesce to form individual phases, which are modeled as oriented ellipsoids at subsequent potentials.

4.2.2 SR-SAXS

The oriented spheroid model fits are shown in Figure 4 and the evolution of the values of $\bar{R}$,

σ and AR during the potential sweep are shown in Figure 5. From the SR-SAXS model fitting, the aspect ratio showed no clear trend with potential and had an average value of 0.75 ± 0.03 . The standard deviation of the size distribution, σ , increases between -0.9 V and -1.0 V on the initial cathodic scan. This increase is only slightly outside of the fit error and could be associated with additional particle nucleation between -0.9 V and -1.0 V. Beyond -1.0 V and into the anodic scan, σ shows very little trend outside of the fit error. Therefore, the width of the particle size distribution does not change within the fit error beyond -1.0 V on the cathodic scan. Keeping in mind that the scattered intensity of a particle scales with the square of its volume[42], it is difficult to resolve smaller particles that nucleate in the presence of larger ones. Therefore, any additional small particles could not be detected beyond -1.0 V. The aspect ratio (and therefore the shape of the particles) remains in the range: 0.75 ± 0.05 , including the fit error shown in Figure 5. The mean radius of the Pb deposit increased from $110 \text{ nm} \pm 2 \text{ nm}$ to $132 \text{ nm} \pm 1 \text{ nm}$ (Figure 5) before the particles began to dissolve at -0.7 V. Therefore, as time passes during the potential sweep, the particle growth is considered to be the primary change in particle morphology, with little change in particle shape and number outside of the fit error. Overall, the mean particle radius increases by $\sim 20 \text{ nm}$ within the potential sweep, which was evaluated at 9 different potentials with SR-SAXS. Referring to Figure 1, $\sim 40\%$ (by time) of this growth occurs during SR-SAXS collection, while the remaining 60% occur after each SR-SAXS collection sequence. Therefore, there is some growth smearing within each SR-SAXS data set, which is not accounted for in Equation 9 and is discussed in the following sub-section. Because of the relatively slow growth kinetics, the growth-smearing is most pronounced just after nucleation (-0.9 V).

4.2.2.a Growth Smearing:

Growth smearing consists of changes in particle size that occurs during all three scans. It is important to note that this phenomena is not specific to SR-SAXS. Rather, it is present for all *in-situ* SAXS measurements where particles are actively growing. The consequence of this effect depends on the growth kinetics and the time of measurement. Here, the particle growth is fastest immediately following nucleation (Figure 5). Therefore, the particle growth is accounted for in the SR-SAXS data collected at -0.9 V, -1.0 V and -1.1 V during the cathodic

scan and compared with Equation 9 to demonstrate this effect. Beyond these potentials, the change in $\bar{R}$ is much less and therefore not evaluated. The difference in the fit parameters with and without including particle growth are greatest at -0.9 V and decrease until the differences are very close to the fit error at -1.1 V.

The total cathodic charge measured during each scan can be used estimate the particle growth. This faradaic charge changes four of the model parameters: the volume fraction, v , aspect ratio, AR , mean radius, $\bar{R}$ and width of the size distribution, σ . Moreover, it is assumed that the particles grow equally in all directions since the value of AR does not change significantly during the potential sweep (Figure 5). The formulation is such that all modifications to the volume fraction, v , $\bar{R}$ and $\bar{H}$ are made to the second and third SAXS profiles obtained at 30° and 20°. Therefore, all other fit parameters are associated with the first SAXS profile (45°) and the values of v , $\bar{R}$ and $\bar{H}$ are modified for the subsequent scans used in the model fitting.

From the chronoamperograms, the total current density passed is converted to Pb volume to give the specific faradaic volume added in the second, $\hat{v}_{F30}$, and third scans, $\hat{v}_{F20}$, by the equations:

$$13. \quad \hat{v}_{F30} = \eta \frac{M}{nFd} \int_{t_0}^{t_{45}} i(t) dt$$

$$14. \quad \hat{v}_{F20} = \eta \frac{M}{nFd} \int_{t_0}^{t_{30}} i(t) dt$$

where η is the faradaic current efficiency ($\eta = 0.7$) for Pb reduction, M is the molecular weight of Pb, n is 2, F is Faraday's constant, d is the density (g cm^{-3}), $i(t)$ is the measured current density and t_0 is the start time of the SR-SAXS set (or first scan), t_{45} is the end time of the first scan (45°) and t_{30} is the end time of the second scan (30°). The units of $\hat{v}_F$ are cm , until it is divided by the mean height of the Pb particles, $\bar{H}$, at which time it is the volume fraction added at the sample angle, α , $v_{F\alpha} = \frac{\hat{v}_{F\alpha}}{\bar{H}_\alpha}$. If we also assume uniform particle growth, the mean radius, $\bar{R}$, must also increase by $\Delta\bar{R}$, which can be calculated from the equations:

$$15. \quad \Delta\bar{R}_{30} = \left[\bar{R}^3 \left[1 + \frac{v_{F30}}{v_{45}} \right] \right]^{1/3} - \bar{R}$$

16.

$$\Delta \bar{R}_{20} = \left[\bar{R}^3 \left[1 + \frac{v_{F20}}{v_{45}} \right] \right]^{1/3} - \bar{R}$$

where v_{45} is a fit parameter and represents the volume fraction at the end of the first scan. Finally, the volume fraction of the second, v_{30} , and third, v_{20} , scans are modified by the equations;

17.

$$v_{30} = v_{45} + v_{F30}$$

18.

$$v_{20} = v_{45} + v_{F20}$$

To evaluate the difference between models with and without growth presented here, the SR-SAXS data at -0.9 V and -1.0 V were fit to the equation:

19.

$$I_{smr}(q_{\perp}, \alpha) = \frac{K_{\alpha}}{\sin \alpha} \int_0^{q_{slit}} I(\mathbf{q}_R(q_{\parallel}, q_{\perp}, \alpha)) dq_{\parallel}$$

20.

$$K_{\alpha} = \frac{v_{\alpha}[1 - v_{\alpha}]\Delta \rho^2 \bar{H}}{T_s}$$

where $\Delta \rho^2$ was taken to be that of Pb in Equation 23. Differences in the parameters, v , $\bar{R}$, σ and AR between Equation 9 and Equation 19 are tabulated in Table 1. It is important to note the scaling correction in Equation 20 that includes T_s and $\bar{H}$, which are used to put $I_{smr}(q_{\perp}, \alpha)$ on an absolute scale. The aspect ratio, AR , is consistently higher than the AR obtained in the original model fit (Figure 5) until -1.1 V where AR is within the range: 0.75 ± 0.05 . On the other hand, the values of $\bar{R}$, σ and v are consistently lower than those obtained without including particle growth, until -1.1 V where the differences are very near the combined fit error. Therefore, the overall effect of growth-smearing is to artificially reduce the aspect ratio and increase the particle size distribution and volume when particle growth is not included in the model fit. The differences in model fit can be seen in Figure 6 and decrease with the order: -0.9 V, -1.0 V and -1.1 V. In general, lower chi-square values were obtained by including the faradaic growth for the Pb-DES system.

4.2.2.b Fit Deviations

The fit of Equation 9 deviates from data at low- q ($q < 0.001 \text{ \AA}^{-1}$) where the model fit is either within or near the measurement error. The source of these deviations is worth some discussion, as they highlight some limitations to SR-SAXS. In the previous section, growth

smearing was discussed and arises due to the relatively long scan times. The model fit represented by Equation 9 also does not account for: particle structure, near-interface solution phases or small surface features. These are aspects of the system which could improve the model fit but are too ambiguous to model with enough certainty.

At very low- q ($q < 0.001 \text{ \AA}^{-1}$), the measured intensity (45° and 30°) increases with q and can be attributed to particle correlations, which influence the scattered intensity at volume fractions greater than ~ 0.06 [42]. However, the absence of a clear peak in intensity, suggests that there is very little order to the deposited particles. Near-interphase phases that were observed in a different DES[25] could not be accounted for in this study. In the previous study, the SR-SAXS from multilayer perturbations could be modeled using a monte-carlo approach. With today's computers, this approach is too computationally expensive for slit-smeared SAXS that spans several decades in q . These perturbations are very anisotropic and might explain the very different small angle scattering at low- q . Finally, it is impossible to differentiate between surface features and isolated particles in the size distribution since the number of particles per aggregate is low. With these considerations in mind, the proposed model is sufficient to extract the change in volume, shape and particle dimensions in the cathodic region of Figure 2.

4.2.2.c Dissolution

From the cyclic voltammogram in Figure 2, one can expect that the Pb phases will dissolve at -0.6 V . Indeed, this is observed in the SR-SAXS. At -0.6 V , the general shape of the scattered intensity remains the same as before but is significantly lower in scale compared with -0.7 V . This rapid decrease in intensity prevents any reliable modeling of the data. Because the shape of the scattered intensity is constant during dissolution, we conclude that the particle aggregates dissolve intact at -0.6 V . At subsequent anodic potentials, no scattering signal, above the background, could be observed.

4.2.3 Electrochemical Impedance Spectroscopy (EIS)

All of the EIS data can be fit to the same equivalent circuit to extract the total surface capacitance and charge transfer resistance at each potential. The model fit of Equation 12 to select EIS data is shown in Figure 7a (cathodic sweep) and Figure 7b (anodic sweep). From each model fit, an average solution resistance, R_s , of $152 \pm 14 \text{ } \Omega$ was observed, while the

charge transfer resistance decreased by an order of magnitude in the presence of the Pb particles. The fit parameters in Equation 12 are used to calculate the overall surface capacitance, C .

For faradaic systems, C , can be calculated from the fit parameters of Equation 12 by the equation:

$$C = \left[Q \left[\frac{1}{R_t} + \frac{1}{R_s} \right]^{\gamma-1} \right]^{1/\gamma} \quad (21)$$

where all parameters are taken from the model fit of Equations 12.[48] All values of C were initially normalized by the area of the working electrode, A_{WE} , to obtain the value of C_{WE} , which is shown in Figure 8. In the range: $0.2 > \Phi > -0.5$, the value of C_{WE} is approximately constant at $8.3 \mu\text{F cm}^{-2}$ on the cathodic sweep and $8.8 \mu\text{F cm}^{-2}$ on the anodic sweep. These values are within $\pm 2 \mu\text{F cm}^{-2}$ of those obtained from the same DES with Hg electrode[28] and a diol-containing DES onto glassy carbon[27]. In both these studies, the differential capacitance behavior[27, 28] in the cathodic regime did not change significantly and therefore the capacitance of the glass carbon, $\hat{C}_{gc}$, is considered to be $8.5 \mu\text{F cm}^{-2}$ throughout the potential region evaluated here. This assumption allows for the removal of the glassy carbon capacitive contribution to C_{WE} .

4.3 Particle Aggregation

The presence of Pb nanoparticles are observed in the SAXS data and shown in Figure 3. In the first 4 minutes, isolated Pb phases are observed without any hierarchal structure. These phases have an R_g of 60 nm, which is a function of both their size and shape[42]. As the particle shape cannot be determined during this time, it is difficult to relate R_g to a physical dimension.

If, for example, the particles are approximately spherical, they would have a radius of 77 nm. In the following scan (6 minutes), these particles have a fractal-like hierarchal structure, which is characterized of a mass-fractal aggregate.[43] The size of these aggregates could not be resolved with certainty but are expected to be greater than $1 \mu\text{m}$, based on the minimum q values evaluated. Based on the volume distribution of the subsequent coalesced particles, a minimum of 1 to 8 particles are expected in each coalesced phase. This relatively low number

density of particles is expected for deposition at low overpotentials [51].

The relatively slow aggregation observed at -0.8 V after electrodeposition was also observed previously with Ag.[25] In the case of Ag, agglomerate scattering dissipated after 3 minutes and the agglomerates were much more compact after 6 minutes with no clear mass fractal scattering. Therefore, the mobility and aggregation of Pb is slower than with Ag at room temperature. Considering the Stokes-Einstein relationship for particle mobility, the higher viscosity in choline:urea DES compared with choline:ethylene glycol[15], as well as larger Pb primary particle sizes both contribute to slower particle transport and aggregation[11]. Once agglomerated, the particles form hard-aggregates and coalesce into a solid phase to minimize the overall surface area[11, 52]. Therefore total coalescence is observed with Pb, rather than partial coalescence.[25]

4.4 Total Volume Fraction Calculation

By combining the electrochemical data and SR-SAXS, it is possible to calculate the overall volume fraction, v_{pb} , of deposited particles and X-ray contrast, $\Delta\rho$. Though this calculation requires some assumptions about the composition of the deposit and the faradaic current, it is useful to obtain reasonable estimates. In order to estimate v_{pb} , the particle deposit is assumed to be pure Pb, though some lead-oxide is expected.[35] In addition, it is assumed that the total current passed at -0.6 V (anodic cycle) represents the faradaic dissolution of Pb or PbO₂. However, from Figure 2, it is known that irreversible cathodic reactions are present, which can cause some dissolution of the Pb deposit at low overpotentials. Therefore, the total volume of deposited Pb, V_{pb} , is considered a minimum value and is calculated by the Equation:

22.

$$V_{Pb} = M \frac{\int_0^{t_{final}} i(t) dt}{zFd}$$

where t_{final} is chosen to be time at which no small angle scattering was observed (-0.5 V), z is 2, M is molecular weight of 207.2 g mol⁻¹ (Pb) or 239.2 g mol⁻¹ (PbO₂) and d is the density of 11.34 g cm⁻³ (Pb) or 9.64 g cm⁻³ (PbO₂). The electrochemical volume fraction is obtained by multiplying the area of the glassy carbon by the volume-mean height of the particles at -0.7 V, which is found by SR-SAXS modeling to be 200 nm. With these assumptions, the volume fraction of deposited lead is estimated to be between 12% (Pb) and 16% (PbO₂) just before

dissolution. These values indicate that the Pb phases are the dilute, scattering phase. However, these values are high enough to expect some structuring in the SR-SAXS data, as mentioned in Section 4.2.2.b.

With the value of v_{pb} known, the X-ray contrast, $\Delta\rho$, can be calculated by the equation:

23.

$$\Delta\rho = \rho_{Pb} - \rho_{DES} = \sqrt{\frac{T_s K}{(v_{Pb} - v_{Pb}^2)\bar{H}}}$$

where K is the scaling constant and $\bar{H}$ is the volume-mean height of the particles at -0.7 V. From the calculation of a minimum value for v_{pb} , the minimum scattering length density of the surrounding solution, ρ_{DES} , is estimated to be $16.7 \times 10^{10} \text{ cm}^{-2}$ (PbO_2) and $18.4 \times 10^{10} \text{ cm}^{-2}$ (Pb). These values are greater than the theoretical scattering length density of the Pb-DES solution, $11.3 \times 10^{10} \text{ cm}^{-2}$. Therefore, immediately following electrodeposition, there is an accumulation of dissolved Pb ions near the glassy carbon surface, as was observed after Ag electrodeposition.[25]

If this elevated concentration is assumed to be constant during the polarization sweep, the volume fraction, v_{pb} , of the Pb deposit is calculated from each model fit by the equation:

24.

$$v_{pb}(1 - v_{pb}) = \frac{T_s K}{\bar{H} \Delta\rho^2}$$

where the lowest root of Equation 24 is the volume fraction of Pb and the deposit is assumed to be elemental Pb. The values of v_{pb} are shown in Figure 9. The value of v_{pb} increases rapidly following nucleation, as both particle growth and some nucleation occur. During the anodic sweep, the particles continue to grow until -0.7 V, where some of the deposit begins to dissolve.

4.5 Specific Capacitance

In the potential range: -0.8 V to -1.2 V, the values of C_{WE} , $\hat{C}_{GC}$ and v_{pb} can be used to obtain the specific capacitance, C_m . First, the total capacitance from the Pb deposit is obtained by removing the capacitive contribution from the glassy carbon. The active area of glassy carbon, in the presence of the Pb deposit, A_{GC} , is obtained by subtracting the cross-sectional area of the Pb deposit from the total area of the working electrode. With knowledge of the volume fraction of the Pb deposit, v_{PB} , A_{GC} is obtained by the equation:

25.

$$A_{GC} = (1 - 3/2 v_{PB}) A_{WE}$$

where any cross-sectional area of the Pb deposit is removed from the total area. Equation 25 assumes that there is no capacitive behaviour between the glassy carbon and Pb deposit. Therefore, the total capacitance of the Pb deposit is obtained by the Equaitons:

$$\begin{aligned} 26. \quad & C_{Pb} = C - \hat{C}_{GC}A_{GC} \\ 27. \quad & C_m = \frac{C_{Pb}}{v_{Pb}A_{WE}\bar{H}d_{Pb}} \end{aligned}$$

where the values of elemental Pb are used, as these values are 10% higher than for PbO₂. The maximum differential capacitance is shown in Figure 10, where C_m has a maximum value at -1.0 V in the anodic and cathodic scans. However, the normalization reveals that C_m is lower in the anodic scan as the specific surface area of the deposit decreases due to coalescence. Because the values of v_{Pb} are minimum value estimates, the values of C_m are therefore maximum values.

The absolute values of C_m are two orders of magnitude lower than typical supercapacitor materials[24], owing to the high density and molecular weight of Pb. The differential capacitance is markedly different than that obtained from a planar Hg electrode, where the capacitance is constant in the cathodic region[28]. It is clear from Figure 3 and Figure 10 that the particle capacitance at -0.9 V is insufficient to achieve electrostatic stability of the Pb particles. From Figure 10, the specific capacitance at -1.0 V, during the cathodic sweep, is higher than that obtained on the anodic sweep. Though this difference is within the experimental error, it is worth noting since particle coalescence is also observed and expected to continue between the two measurements. This coalescence is expected to reduce the total available area of the Pb particles. Therefore, the specific differential capacitance shown in Figure 10 reveals an optimum potential for stable nanoparticle electrodeposition, as well as particle coalescence.

The SAXS data following electrodeposition at -1.0 V and -0.8 V, at 30° sample angles, are shown in Figure 11. These scattering curves revel a Guinier region that is much smaller than at -1.0 V than at -0.8 V. Using the Guinier approximation, the particles obtained at -1.0 V have an R_g of 36 nm, compared with 58 nm obtained at -0.8 V. However, due to time constraints, the sample was not able to be polarized for long enough to observe any aggregation. Despite this, it is clear from the differential capacitance measurements that the highest surface charge, and therefore the best chance of achieving electrostatic stability, is

obtained at -1.0 V.

4.6 SR-SAXS Approach

The SR-SAXS approach presented in this study was necessary to resolve the moderate particle anisotropy ($AR < 1$) because of the Bronse-Harte instrument geometry. This geometry is able to resolve lower q values (typically, $q < 0.001 \text{ \AA}^{-1}$) compared with a pinhole SAXS setup, but only provides the scattered intensity in one dimension. If it were possible to perform these experiments on a pinhole SAXS setup, multiple sample rotations may not be necessary with such a simple SAS model. Instead, one could use GTSAXS. This approach would be necessary if one were to use a lower flux X-ray source, which requires longer counting times. There are also different possible formulations of the SR-SAXS approach. For example, if the system is sufficiently reversible, it may be possible to make multiple potential sweeps at a single sample angle. However, this approach would require more time and one must be confident that the nucleation and growth kinetics are the same from one sweep to the next.

5. Conclusions

For the model Pb nanoparticle system, complementary suites of SR-SAXS and electrochemical techniques were used to obtain key physical and electrochemical properties of the Pb nanoparticles. This approach was discussed in detail and provides an experimenter with the ability to obtain: the size and shape of surface bound phases, the volume fraction of the surface scattering phase, as well as the specific differential capacitance of the particle deposit. The proposed approach is valid for systems where growth kinetics are sufficiently slow over the data collection period. In cases where this is may not be true, the faradaic charge can be used to estimate the effect of growth during data collection and was discussed in detail. With the calibration of the SR-SAXS data, an elevated scattering length density of the surrounding solution was obtained from the model fitting, as reported previously for Ag. This increased scattering length density indicates a high concentration of the dissolved metal precursor exists near the surface, following electrodeposition.

The differential surface capacitance reveals that the optimum potential for electrodeposition of stable Pb particles is -1.0 V. Below this overpotential (-0.8 V), the surface charge on the Pb particles is insufficient to thwart aggregation, which was observed by SAXS over the

1 course of 6 minutes. These aggregates coalesce into moderately oblate features, whose
2 dimensions were resolved by SR-SAXS. These oblate shapes were a consequence of 2-D
3 aggregation and coalescence that was also resolved by SAXS immediately following
4 nucleation. Where the differential capacitance is not constant in the cathodic region, the
5 combined X-ray scattering, electrochemical approach used here can also be used to obtain the
6 optimal particle capacitance to achieve smaller and nanoparticles that have a higher surface
7 charge and therefore more likely to be electrostatically stable.
8
9

10 **Acknowledgments**

11 This research used resources of the Advanced Photon Source, a U.S. Department of Energy
12 (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne
13 National Laboratory under Contract No. DE-AC02-06CH11357. This study was also partially
14 funded by Lawrence Livermore National Laboratory under Contract No.
15 DE-AC52-07NA27344. The authors would like to thank Dr. Andrew Allen for his very
16 helpful comments and suggestions.
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Tables

Parameter	-0.9 V	-0.9 V (with growth)	-1.0 V	-1.0 V (with growth)	-1.1 V	-1.1 V (with growth)
$\bar{R}$ (nm) $\pm$ 2 nm	110.9	45° = 101.3 30° = 102.0 20° = 103.1	117.6	45° = 109.2 30° = 109.6 20° = 110.3	122.9	45° = 117.2 30° = 117.6 20° = 118.2
σ (nm) $\pm$ 2 nm	56.4	52.2	63.4	59.0	60.4	57.8
$AR \pm 0.02$	0.72	0.81	0.76	0.82	0.75	0.79
$\nu \pm 1.1\%$ (10%)	0.056	45° = 0.052 30° = 0.053 20° = 0.055	0.076	45° = 0.073 30° = 0.074 20° = 0.076	0.089	45° = 0.087 30° = 0.087 20° = 0.089

Table captions

Table 1 compares the SR-SAXS model fit parameters from the Equation 9 (second, fourth and sixth columns) with those obtained by including particle growth in Equations 19 (third, fifth and seventh columns). Errors associated with all the parameters were obtained from the Jacobian matrix in the least-squares fitting. The errors in parenthesis that are associated with ν were taken from the Figure 8 and are larger due to the uncertainty in the phase of the Pb deposit.

Figure Captions

Figure 1 is a plot of the measured potential versus time (red) for one of the potentials (-0.9 V) during the potential sweep procedure described in the Experimental section 2.4. The black triangles are the times at which SAXS data collection finished for each sample angle shown with the blue sample cells. The inset is a simplified schematic showing the scattering vectors used in the sample geometry.

Figure 2 contains three consecutive cyclic voltammograms of the Pb-DES system. The potential was $I_c R$ corrected using the mean resistance of 152Ω obtained from the EIS fitting.

Figure 3 is a log-log plot of the SAXS data collected at sample angles of 45° (green), 30° (blue) and 20° (red). The Unified Equation fits for the non-aggregated particles (black dash) and aggregated particles (black sticks) were used to obtain the mean size of the Pb deposit that aggregate into larger aggregate structures.

Figure 4 is a log-log plot of the background-subtracted SR-SAXS data (right) collected in the potential range where the Pb deposit can be observed. The data (colored) and model fits (black) are shown on the log-log plot to the left. The sample cell orientations for each curve are shown in blue.

Figure 5 shows the potential evolution of the particle size during the potential sweep. The evolution in the size distribution, σ , and aspect ratio are shown in the inset, with very little change over the course of the experiment. The cathodic cycle is shown in blue, while the anodic cycle is shown red. The error bars in Figure 5 were obtained from the jacobian matrix in the least-squares fitting routine.

Figures 6a, 6b and 6c are log-log plots showing the difference in model fits with (solid line) and without (dashed line) faradaic growth for the SR-SAXS data collected at -0.9 V, -1.0 V, and -1.1 V, respectively. Each SR-SAXS data set consists of SAXS data collected at 20° (red), 30° (blue) and 45° (green).

Figure 7a and 7b contain the EIS data (markers: square is the modulus and circle is the phase) and models (line) from the cathodic and anodic sweeps, respectively. The selected data from: 0.2 V (red), -0.9 V (green), -1.0 V (black) and -1.1 V (blue) are shown in each.

Figure 8 is a plot of the differential capacitance obtained from the EIS modeling in the potential range: 0.2 V to -1.2 V. The cathodic cycle is shown in blue, while the anodic cycle is shown red. Error bars were obtained from model fitting of the EIS data.

Figure 9 is a plot of the volume fraction obtained from combining the SR-SAXS modeling with the total anodic charge passed at -0.6 V. Error bars were obtained from the error in the fit parameters obtained by the SR-SAXS modeling, as well as the error associated with the uncertainty in phase (i.e. pure Pb or pure PbO_2).

Figure 10 is the differential specific capacitance plot obtained by normalization of the deposit mass. The values in blue represent the cathodic scan, while values in red represent the anodic scan. Error bars in the calculation of C_m account for model fitting errors in both the EIS and

SR-SAXS modeling.

Figure 11 is a log-log plot showing the SAXS data collected at sample angles of 30° and 4 minutes after electrodeposition at -0.8 V (closed squares) and -1.0 V (open circles). Comparison of the two data show that smaller particles are obtained at -1.0 V.

Figure1

Figure2

Figure3

Figure4

Figure5

Figure6

Figure 7

Figure8

Figure9

Figure10

Figure11