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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 $2.5 +/- 0.5\,F\,g^{-1}$ 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*.

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

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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