Application of the combined electrochemical quartz crystal microbalance and probe beam deflection technique in deep eutectic solvents

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ABSTRACT

The electrochemical quartz crystal microbalance (EQCM) and probe beam deflection (PBD) have been widely used to study interfacial processes in molecular solvent-based electrolytes. However, there has been limited use of the EQCM and none of PBD in room temperature ionic liquids, including deep eutectic solvents (DES). Here we explore the use of the combined EQCM/PBD technique to the study of Ag and Sn electrodeposition from a DES comprising a 1:2 mixture of choline chloride and ethylene glycol. While overcoming the effect of viscous loss in the acoustic wave (EQCM) part of the experiment is understood, the optical (PBD) technique fails to provide a meaningful response in slow scan rate voltammetric experiments; this contrasts sharply with the straightforward behaviour seen in aqueous media. Solution transport considerations reveal this to be a consequence of long surface-to-beam transit times in the viscous DES. The problem can be overcome by operating at scan rates 1-2 orders of magnitude slower, permitting application of this powerful technique to novel media of technological interest. The PBD responses reveal unanticipated chemical effects: multiple complexes in the Ag system and solubility limitations in the Sn system, neither of which is evident from the electrochemical or QCM responses.

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1. Introduction

The electrochemical quartz crystal microbalance (EQCM) [1–3] and probe beam deflection (PBD) [4–6] techniques have individually proved to be extremely useful probes of interfacial processes that involve exchange of chemical species between an electrode surface and its ambient electrolyte solution. These encompass such diverse processes as electropolymerization [7–11], electrocrystallization [12], adsorption [13,14], absorption [15], underpotential deposition (UPD) [16,17] and electroactive film redox switching [8,18–25]. Since the EQCM, in the simplest and most commonly used mode, is a gravimetric probe, it is sensitive to the transfer of neutral species (notably solvent) and has high sensitivity to the deposition and dissolution of heavy species, notably metals. However, it is predictably less sensitive to light species: the extreme case is the transfer of protons to/from an electroactive film in order

to maintain electroneutrality [26]. The physical basis of the PBD technique is associated with a gradient of refractive index, so its sensitivities to various species are quite different to that of the EQCM; for example, interfacial proton transfers may be detected readily [27] but solvent transfer much less so.

It is quite clear from the above considerations that a combination of the EQCM and PBD techniques promises considerable power and sensitivity. Strictly, since the electrochemical and acoustic ("E" and "QCM") measurements are separate, there are three measurands in a typical EQCM/PBD experiment: current (or charge), mass and optical deflection. Consequently, by combining the outputs of the three simultaneous experiments, this holds the promise of resolving the transfers of up to three species, for example the anion and cation of the electrolyte and solvent [28,29]. That this is the case has been demonstrated for metal electrodeposition under UPD [30] or bulk [31] conditions and electroactive polymer film redox switching [32].

Interestingly, all the above studies used conventional electrolytes, based on molecular solvents typified by water or acetonitrile. Recently, there has been considerable interest in the

use of a range of room temperature ionic liquids (RTIL) [33] and deep eutectic solvents (DES), for example based on quaternary ammonium salts (QAS) and hydrogen bond donors (HBD) [34,35]. Interest in the use of these novel media is provoked by both practical and fundamental aspects. In the former instance, they offer very high ionic concentrations (e.g. high ion availability for charge storage applications), wide potential windows, excellent solvating power for a wide range of electroactive species and low environmental impact. These attributes have generated considerable attention in the literature for applications involving metal plating and related electrodeposition processes, where they provide practical alternatives for aqueous-based formulations that involve toxic or otherwise environmentally unacceptable components [36].

In the latter instance, the notion of a medium that is exclusively ionic (at ambient conditions) is extremely interesting. In the context of electroactive polymer films, molecular solvents have been shown to play a major role in controlling viscoelastic properties and thence film mechanical behaviour and ion transport rates. Consequently, the removal of such species from the system suggests that interesting and novel effects might be observed.

These ideas motivate the use of the EQCM/PBD technique to study electrochemical processes involving RTIL and DES media. Based on the phenomena underlying the QCM and PBD techniques, accomplishing this will require consideration of the *physical* (*cf. chemical*, above) characteristics of these media. Specifically, the very high viscosities of some RTIL/DES systems (1-3 orders of magnitude greater than water or typical organic solvents) may be expected to increase damping (energy dissipation) of the QCM crystal resonance and to diminish the fluxes of species to/from the interface. From the perspective of PBD, the notion of local changes in "electrolyte concentration" ceases to have the same physical meaning and some simple considerations of molar refractivity of the components suggests that the refractive index gradients (and thence optical deflections) may be smaller.

There are clearly significant opportunities but also substantive challenges in the application of the EQCM/PBD methodology to interfacial processes involving RTIL and DES media. The generic goals of the present study are to identify which of the challenges identified above is predominant and, *via* appropriate instrumental and analytical interventions, to resolve them in order that the combined EQCM/PBD technique can be implemented in these fundamentally and technologically interesting media. While there are a few reports of the EQCM being used to study electrochemical processes in RTILs, these are predominantly the less practicable imidazolium-based [37,38] or pyrrolidinium-based [37,39,40] systems and there are few studies in DES media [41,42]. To the best of our knowledge, neither the PBD technique nor the combined EQCM/PBD technique has been used to study interfacial processes in RTILs or DESs. The generic aim of this work is to overcome the practical measurement challenges presented by these systems. As we shall show, this creates the opportunity for novel fundamental studies of practical significance in electrochemically controlled aspects of energy storage, materials science, corrosion protection and metal finishing.

2. Experimental

2.1. Materials

AgNO$_3$, AgCl, SnCl$_2$, choline chloride and ethylene glycol (Sigma Aldrich) were used as received. The DES was formed by mixing the QAS (choline chloride, which we represent as Ch$^+$Cl$^-$) with the HBD (ethylene glycol, which we represent as EG) in a 1:2 molar ratio. We will use the shorthand notation Ch$^+$Cl$^-$(EG)$_2$ for this formulation. (Note: it is sometimes referred to as *Ethaline 200* [41]; the number

denotes the stoichiometry which, in this instance, results in complexation of the anion by the ethylene glycol such that there are no free neutral molecules.)

2.2. Instrumentation

The electrochemical cell comprised a standard three-electrode configuration mounted inside an optical glass cuvette (Hellma, $42 \times 42 \times 30$ mm). A 10 MHz AT–cut Au plated quartz crystal working electrode (ICM Manufacturing, Oklahoma City, USA, piezoactive area 0.21 cm^2), was mounted on the end of a glass tube. The counter electrode was an Ir-coated Ti mesh (area 5.50 cm^2). An Ag/AgCl wire exposed to the chloride-containing DES medium was used as a reference electrode; this has previously been shown to provide a stable reference potential in choline chloride-based eutectics [43].

The electrochemical, gravimetric and optical signals were recorded simultaneously using a Gamry Reference 600 potentiostat integrated with Gamry eQCM 10 M micro-gravimeter. The potentiostat was coupled to a home-built optical deflection system based on that described previously [31]. The optical deflection measurements were conducted using a dual photodiode which was set 18.5 cm from the electrochemical cell, resulting in a position sensitivity of 0.44 μrad/mV.

2.3. Procedures

Silver was deposited/dissolved potentiodynamically by cycling the applied potential between 0.2 and -0.3 V at potential scan rates in the range 2.5 - 10 mV s^{-1} in aqueous electrolyte (0.001 M AgNO$_3$/0.2 M HClO$_4$) and 0.0625–0.5 mV s^{-1} in Ch$^+$Cl$^-$(EG)$_2$ (containing 0.01 M AgCl). A similar procedure was used for the tin system (0.01 M SnCl$_2$ in Ch$^+$Cl$^-$(EG)$_2$), but with potential limits of -0.34 and -0.68 V and scan rates in the range 0.03125–0.25 mV s^{-1}. All measurements were made at room temperature (20 ± 2 °C).

2.4. Data analysis

Interpretation of the QCM frequency response took into account two factors. First, the solution is purely viscous; there is no storage component to the complex modulus. Second, the similar values of the resonant admittance for bare and for polymer-coated electrodes immersed in the DES demonstrate that there is no significant viscous loss associated with the film, i.e. the loss modulus is much less than the storage modulus. Thus, the films of the thickness used here are acoustically thin (in common parlance "rigid", although this is not accurate use of the terminology [1],[3]). Consequently, the frequency response can be interpreted in gravimetric terms using the Sauerbrey equation [44]. This is the case for both the Ag and Sn systems. Additionally "calibration" data for Ag deposition are provided *via* the mass-charge relationship in both integral (Δm-Q) and differential ($\delta(\Delta$m)/δt-i) variants.

The angular deflection (θ) of the laser beam by the interfacial concentration gradient perpendicular to the surface, $\delta c(x,t)/\delta x$, is described by:

$$\theta(x, t) = \left(\left(\frac{1}{n} \frac{\delta n}{\delta c} \right) \left(\frac{\delta c(x, t)}{\delta x} \right) \right) \quad (1)$$

where l is the interaction length of the light beam with the surface (here, the electrode diameter), x is the distance of the laser beam from the electrode surface and ($\delta n/\delta c$) represents the variation of refractive index (n) with concentration (c). The laser beam is deflected toward the region of higher refractive index. The instrument was set up such that a positive (negative) deflection represents decreasing (increasing) refractive index at the surface