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Estimation of electrochemical quartz crystal microbalance frequencies from cyclic voltammetric data:—underpotential deposition of metals as an illustration

Abstract The estimation of electrochemical quartz crystal microbalance (EQCM) frequencies from a given cyclic voltammetric data is analysed using underpotential deposition (UPD) of metals as an illustrative process. The crucial role played by the surface roughness of electrodes and electrosorption valency of the depositing species is pointed out. The computed EQCM frequency shifts for the UPD of Cd and Tl on polycrystalline Ag electrodes are in satisfactory agreement with the experimental data.

Keywords Electrochemical quartz crystal microbalance · Cyclic voltammetry · Underpotential deposition · Surface roughness · Electrosorption valency

Introduction

Among several electrochemical techniques available for detecting nanomolar changes of adsorbed species at electrode surfaces, piezoelectric microgravimetry (employing electrochemical quartz crystal microbalance (EQCM)) plays a central role in diverse contexts such as redox behavior of conducting polymers [1, 2] corrosion studies of alloys [3], investigation of thin solid films of fullerenes [4], specificity of protein binding [5], underpotential deposition(UPD) of metals [6, 7] etc. Interestingly, these studies also employ cyclic voltammetric techniques for obtaining new insights regarding the mechanism of charge transfer. However, the estimation of EQCM frequencies [8, 9] starting from the *experimental* cyclic voltammograms is a non-trivial exercise. The demonstration of such a one-to-one correspondence becomes essential not only to extend the scope of EQCM but also to comprehend the interfacial phenomena of interest.

The bottlenecks that arise in this context are many; among them, mention may be made of the following: (1) The current–potential responses in cyclic voltammetry pertaining to all mechanistic schemes are usually provided as tabular compilations rather than explicit parametric representations, (2) the information sought from the cyclic votammograms are themselves dependent upon the mechanism of the electron transfer and (3) the EQCM measures the mass changes of a desired species in contrast to cyclic voltammetry which yields current as a function of potential and sweep rate.

In this article, we suggest a methodology of deducing EQCM data from cyclic voltammograms using UPD of metals as an illustrative system. The central feature of the analysis consists of the estimation of charge densities incorporating the roughness factor of the electrodes and partial charge transfer characteristics of the depositing species from the experimental current–potential response.
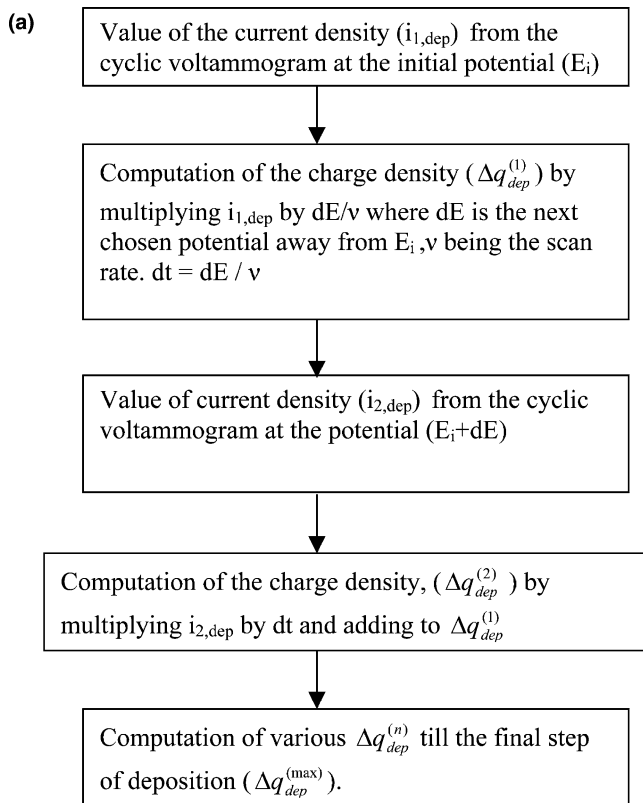
Methodology for estimating the frequency changes of EQCM from cyclic voltammetry

Since the frequency shifts pertaining to EQCM data are written in terms of the corresponding mass changes, it is imperative that the latter should be formulated using the parameters of the cyclic voltammograms. An obvious choice to accomplish the same is the evaluation of appropriate surface excess corresponding to the charge densities from the experimental current–potential response. This is then converted into mass changes with the help of parameters such as the electrosorption valency, roughness factors, etc., as shown in the following section.
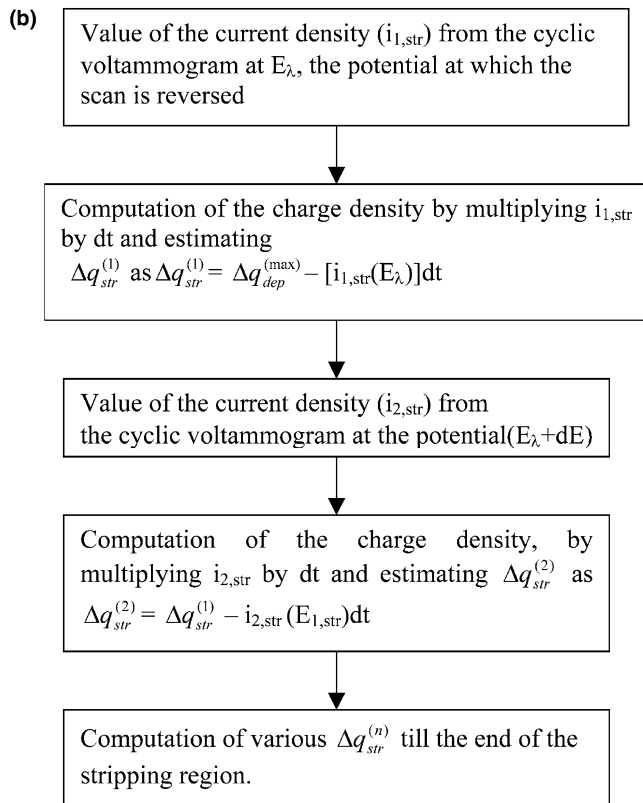
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Estimation of charge densities for deposition and stripping

The estimation of charge densities from the corresponding current–potential data appears prima facie, a trivial exercise. However, a systematic identification of various parameters constituting the phenomena is required, depending upon the process under consideration. In the case of UPD, the charge densities for deposition and stripping may be computed as shown in Scheme 1 [10]. The potential scale of the cyclic voltammogram is converted into time scale using the relation [11] $dt = dE / \nu$ where dE denotes the difference between two potentials chosen, ν being the scan rate. For the initial potential E_i, the corresponding current density is denoted as $i_{1,dep}$. This, after multiplying by dt, yields $\Delta q_{dep}^{(1)}$, which is the charge density till that instant of time (vs potential). Scheme 1a, 1b depicts the successive computation of charge densities till the end of the deposition and stripping processes, respectively.

(a)

Value of the current density ($i_{1,dep}$) from the cyclic voltammogram at the initial potential (E_i)

↓

Computation of the charge density ($\Delta q_{dep}^{(1)}$) by multiplying $i_{1,dep}$ by dE/ν where dE is the next chosen potential away from E_i, ν being the scan rate. $dt = dE / \nu$

↓

Value of current density ($i_{2,dep}$) from the cyclic voltammogram at the potential (E_i+dE)

↓

Computation of the charge density, ($\Delta q_{dep}^{(2)}$) by multiplying $i_{2,dep}$ by dt and adding to $\Delta q_{dep}^{(1)}$

↓

Computation of various $\Delta q_{dep}^{(n)}$ till the final step of deposition ($\Delta q_{dep}^{(max)}$).

Scheme 1 (a) Steps involved in the estimation of charge densities during the underpotential deposition process. (b) Steps involved in the estimation of charge densities at various potentials during stripping.

(b)

Value of the current density ($i_{1,str}$) from the cyclic voltammogram at E_λ, the potential at which the scan is reversed

↓

Computation of the charge density by multiplying $i_{1,str}$ by dt and estimating $\Delta q_{str}^{(1)}$ as $\Delta q_{str}^{(1)} = \Delta q_{dep}^{(max)} - [i_{1,str}(E_\lambda)]dt$

↓

Value of the current density ($i_{2,str}$) from the cyclic voltammogram at the potential($E_\lambda+dE$)

↓

Computation of the charge density, by multiplying $i_{2,str}$ by dt and estimating $\Delta q_{str}^{(2)}$ as $\Delta q_{str}^{(2)} = \Delta q_{str}^{(1)} - i_{2,str}(E_{1,str})dt$

↓

Computation of various $\Delta q_{str}^{(n)}$ till the end of the stripping region.

Scheme 1 (Contd.)

Estimation of charge densities for deposition and stripping

For accurate estimation of the surface coverages, it is essential to incorporate the roughness of the electrode surface. In general, the electrode surfaces are not homogeneous and hence are not ideally smooth. Non-uniform distribution of metal oxides are often found on metal surfaces and pretreatment procedures also introduce roughness. The frequency shifts obtained from EQCM are also affected by the roughness of the substrate employed. Thus, inclusion of roughness factors in the computation of charge densities becomes essential. Hence, in order to obtain a correspondence between cyclic voltammetry and EQCM data, the true surface charge densities are obtained by multiplying the charge densities measured from cyclic voltammetry by roughness factor, R, of the working electrode surface. The roughness factor of the electrodes may be obtained via independent experiments [12] and model considerations [13]. Hence, for the deposition process, we formulate

$$\Delta q_{\text{truedep}}^{(1)} = R[i_{1,\text{dep}}(E_i)]dt = R\Delta q_{\text{dep}}^{(1)} \tag{1}$$

$$\Delta q_{\text{truedep}}^{(2)} = R[i_{2,\text{dep}}(E_{1,\text{dep}})]dt + \Delta q_{\text{truedep}}^{(1)} \tag{2}$$

while the expressions for the stripping process becomes

$$\Delta q_{\text{truedep}}^{(1)} = \Delta q_{\text{dep}}^{(\text{max})} - R[i_{1,\text{str}}(E_\lambda)]\text{d}t \quad (3)$$

$$\Delta q_{\text{truestr}}^{(2)} = \Delta q_{\text{truestr}}^{(1)} - R[i_{2,\text{str}}(E_{1,\text{str}})]\text{d}t \quad (4)$$

The conversion of these true charge densities into mass changes requires incorporation of the electrosorption valency γ—a measure of the partial charge transfer, that is,

$$\Delta m_{\text{dep}}^{(n)} = \Delta q_{\text{truedep}}^{(n)} \left(\frac{M}{\gamma F}\right) \quad (5)$$

and

$$\Delta m_{\text{str}}^{(n)} = \Delta q_{\text{truestr}}^{(n)} \left(\frac{M}{\gamma F}\right) \quad (6)$$

where M and F denote, respectively, the molar mass and Faraday constant. The well known Sauerbery equation [14] relates the EQCM frequency shift (Δf) to the mass changes (Δm) as

$$\Delta f = -\frac{2\Delta m f_0^2}{nA\sqrt{\mu\rho}} \quad (7)$$

where f_0 denotes the fundamental frequency of the crystal, n is the order of the harmonic while μ represents the shear modulus (2.947×10^{11} g cm^{-1} s^{-2}), A is the projected area of the electrode, ρ being the density of the quartz (2.648 g cm^{-3}). Substitution of eqs. 5 and 6 in Eq. 7 yields the frequency changes as

$$\Delta f_{\text{dep}}^{(n)} = -\frac{2\left(\Delta q_{\text{truedep}}^n(E)M/(\gamma F)f_0^2\right)}{nA\sqrt{\mu\rho}} \quad (8)$$

and

$$\Delta f_{\text{str}}^{(n)} = -\frac{2\left(\Delta q_{\text{truestr}}^n(E)M/(\gamma F)f_0^2\right)}{nA\sqrt{\mu\rho}} \quad (9)$$

pertaining to deposition and stripping, respectively. For a 5 MHz resonating quartz crystal operating in the fundamental mode, the constant K defined as $K = (2f_0^2)/nA\sqrt{\mu\rho}$ has a value of 5.66×10^7 g^{-1} cm^2 Hz.

Results and discussion

As mentioned earlier, EQCM in conjunction with cyclic voltammetry has been employed in diverse contexts. However, for illustrating the elucidation of EQCM data from the corresponding cyclic voltammograms, it is appropriate to choose systems that are simple but nevertheless illustrate the essential features. In view of this, the UPD systems of (1) Cd on Ag and (2) Tl on Ag are considered which do not exhibit competitive adsorption of anions [15] and/or two-dimensional phase transitions [16, 17].

The crucial parameters of our model analysis are (1) roughness factor of the electrode and (2) electrosorption valency. Among several methods available for estimating the roughness, mention may be made [12] of evaluation of (1) the charge corresponding to the reduction of oxides formed at different reversal potentials (2) the pseudocapacitance of the electrical double layer and (3) constant phase element (CPE) in ac impedance measurements.

The roughness factor of electrode surfaces in cyclic voltammetry depends upon the pre-treatment procedures and for a given substrate, a common value for roughness factor is employed and dictated by the experimental protocol. Consequently, a potential-independent roughness value has been employed here. The roughness factor (R) is the ratio of the real area to the geometrical area of the electrode surface. Real area corresponds to the total area which is inclusive of the kinks and valleys present on the electrode surface which subsequently produces roughness. The liquid confined in these rough cavities is dragged along while the crystal surface oscillates. Hence, by including the value of R in the estimation of true charge density at each potential (i.e., $\Delta q_{\text{true}}^{(n)} = R[i_{n,}(E)]\text{d}\,t + \Delta q_{\text{true}}^{(n-1)}$), the effect of liquid enclosures in the roughened surfaces is also taken into account since the true charge density, $\Delta q_{\text{true}}^{(n)}$, is a simultaneous measure of the charge due to the UPD of metal ions and the effect of liquid entrapped in the pores of the rough surface. Hence, the estimated frequency shift denotes the combined effect of both the above quantities.

The electrosorption valency (γ) is a measure of the partial charge transfer of the adsorbate and plays a crucial role in ionic adsorption as well as chemisorption of neutral organic compounds. This concept has served as a touchstone for quantum theory of charge transfer processes at electrode surfaces. The customarily employed definition of γ originally due to Schultze and Vetter [18] is

$$\gamma = -\frac{1}{F}\left(\frac{\partial q^M}{\partial \Gamma_{\text{ad}}}\right)_E$$

where q^M and Γ_{ad} denote respectively charge density and surface concentration of the specifically adsorbed species and E is the applied potential. In general, γ is a function of applied potential. However, the potential dependence of γ varies from one system to the other. In our present context, the introduction of γ becomes essential in so far as the UPD involves the partial charge transfer of the adsorbate. In our illustrative examples, the influence of potential on γ has explicitly been reported only for UPD of Tl on Ag. In the other example, i.e., UPD of Cd on Ag, a constant value of γ over the entire potential region has been reported earlier [19] and has been employed by us. However, depending upon the system under consideration, the detailed influence of γ on EQCM frequencies needs to be investigated.

Fig. 1 **a** Cyclic voltammogram for the underpotential deposition of Tl on Ag in 0.1 M Na_2SO_4 and 10 mM Tl^+ at pH 5 at a scan rate of 10 $mV\ s^{-1}$ from [19]. **b** The variation of the charge density with potential, during **a** deposition (*solid black line*) and **b** stripping (*dashed black line*) deduced from **a** employing Eqs. 1, 2, 3, and 4 of the text. **c** The EQCM response depicting the variation of the frequency shift with potential, for UPD of Tl on Ag. curves (*i*) and (*ii*) depict the frequency response for deposition and stripping respectively using reported estimates of γ in different potential regions of UPD [21]. *Solid line* corresponds to the experimental data of [19] while the circles are obtained using Eq. 8 for deposition and Eq. 9 for stripping. **d** The EQCM response depicting the variation of the frequency shift with potential, for UPD of Tl on Ag. curves (*iii*) and (*iv*) depict the frequency response for deposition and stripping respectively using $\gamma = 1$. Solid line corresponds to the experimental data of ref. [19] while the circles are obtained using Eq. 8 for deposition and Eq. 9 for stripping
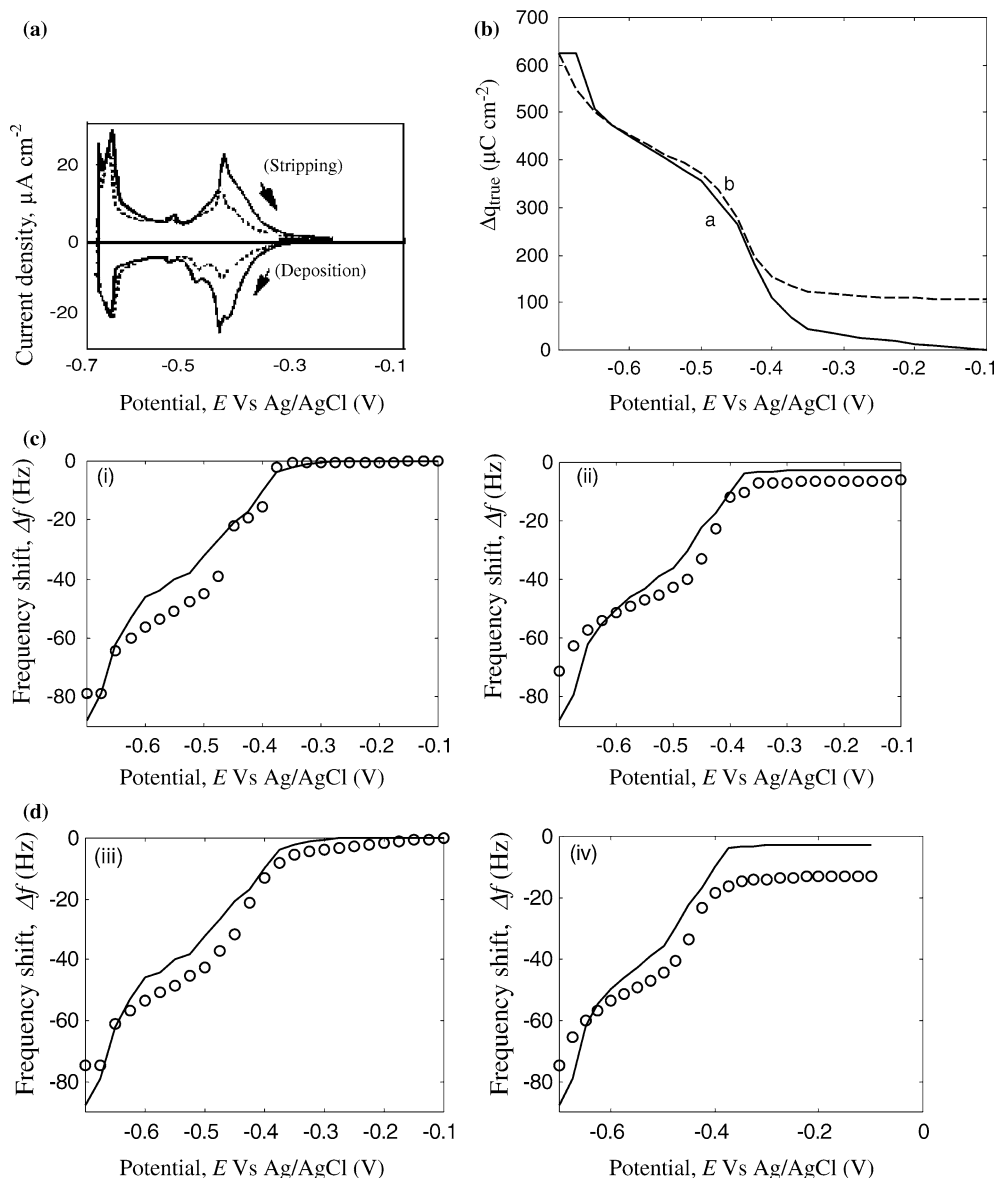

UPD of Tl on Ag

Figure 1a depicts the cyclic voltammogram pertaining to the UPD of Tl on Ag in an aqueous solution of 0.1 M Na_2SO_4 [19]. The current densities at various potentials were deduced with the help of GIMP software [20] and then Δq_{true} vs E plot (Fig. 1b) is generated[1] using Scheme

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[1]Figures 1c and 3c from ref. [19] depict the surface coverages as a function of potential albeit only the deposition process. Surface coverage, θ, is defined as $\theta_i = \Delta q^i_{dep}/q_{max}$ where $q_{max} = ze/(2r)^2$, z denotes the valency of the species, e is the electronic charge, Δq_{dep} is the charge density corresponding to the appropriate potentials evaluated using Eqns. 1 and 2 and r is the ionic radii of the depositing species [23] ($r = 0.95$ Å for Cd^{2+} and 1.5 Å for Tl^+. The plots of surface coverage, θ vs E plot so deduced are in excellent agreement with those of Ref. [19], thus validating the Scheme 1 for computing charge densities.

1. The EQCM shifts at various potentials are given in Fig. 1c. UPD of Tl on Ag is completely reversible at all the potentials and the reversibility has further been demonstrated recently by radiotracer studies [21]. Hence, the roughness factor is identical during the deposition and stripping process. A value of 1.5 for R [12] is employed in Eqs. 8 and 9 with the molar mass of Tl being 204.4 $g\ mol^{-1}$. In a study of this system [22] using EQCM data, various mean values of γ have been deduced for different potential regions, viz., 1.28 ($-0.1\ to\ -0.4\ V$), 0.95 ($-0.4\ to\ -0.45\ V$) and 0.85 ($-0.45\ to\ -0.7\ V$) for deposition process and 2.06 ($-0.1\ to\ -0.35\ V$), 1.55 ($-0.35\ to\ -0.4\ V$), 1.02 ($-0.45\ to\ -0.475\ V$) and 1.05 ($-0.475\ to\ -0.7\ V$) in the case of stripping. In another investigation [21], the electrosorption valency for this system has been reported to vary from zero to unity for the entire potential region. This implies that the precise values of γ are uncertain. Consequently, the EQCM shifts

Fig. 2 **a** Cyclic voltammogram for the underpotential deposition of Cd on Ag in 0.1 M Na_2SO_4 and 6 mM Cd^{2+} at pH = 5 at a scan rate of 10 mV s^{-1} from ref. [19]. **b** The variation of the charge density with potential, during **a** deposition (*solid black line*) and **b** stripping (*dashed black line*) deduced from **a** employing Eqs. 1, 2, 3, and 4 of the text. Roughness factor, $R = 1.5$ for deposition and 1.8 for stripping. **c** The EQCM response depicting the variation of the frequency shift with potential, for UPD of Cd on Ag. *Solid line* corresponds to the experimental data of [19] while the circles are obtained using (**a**) Eq. 8 for deposition and (**b**) Eq. 9 for stripping
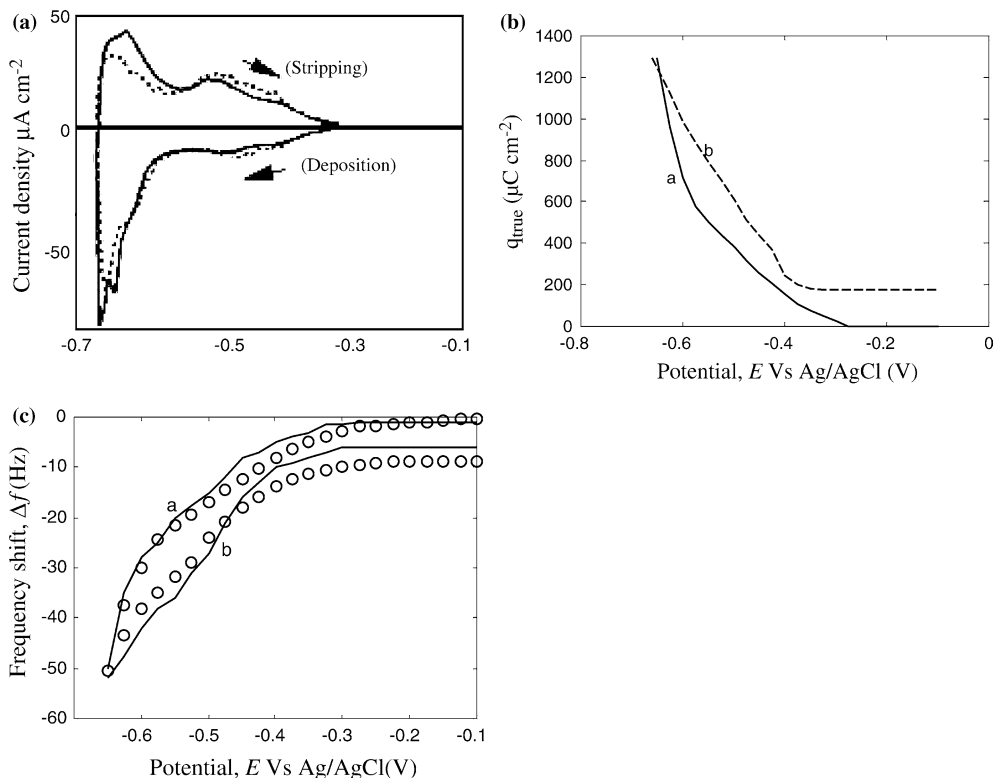
computed using the various ranges of γ shown above as well as a constant value of unity are depicted in Figs. 1c, 1d. It may be noted that the EQCM response obtained with varying γ values yields a more satisfactory agreement with the experimental values. In order to avoid overlapping, the EQCM frequency shifts for the deposition and stripping are shown separately.

UPD of Cd on Ag

Figure 2a depicts the cyclic voltammogram (CV) pertaining to the UPD of Cd on polycrystalline Ag in an aqueous solution of 0.1 M $HClO_4$ [19]. The charge densities and mass changes for the UPD of Cd on Ag electrodes are computed as in the earlier case. The corresponding Δq_{true} vs E plot for UPD of Cd on Ag is shown in Fig. 2b. The choice of roughness factor for this system is more subtle. The value of the roughness factor during deposition and stripping is not equal [24, 25] in this case. For example, in the case of UPD of Cd and Tl on Ag, the same substrate has been employed and hence the roughness factor is identical for the two systems during deposition. However, during stripping, only for perfectly reversible systems most of the deposited atoms will be stripped off from the substrate and hence the roughness factor for deposition will equal that for stripping. In the case of UPD of Tl on Ag [19], the deposition and stripping curves are mirror images of each other in the entire region of the cyclic voltammogram indicating a perfectly reversible behaviour leading to the inference that the roughness factor is identical for both deposition and stripping. On the other hand, it is anticipated that for the UPD of Cd on Ag, different R values are required for the two regions. A value of 1.5 for R has been employed for estimating the true charge densities during deposition and $R = 1.8$ is used for the stripping process. A higher value of R is chosen on account of the Cd–Ag alloy formation during the deposition of Cd on Ag as demonstrated elsewhere [26, 27]. Further, the alloy undergoes dissolution leading to pitting of Ag on account of stripping of Cd which enhances the roughness factor. A value of 1.7 is employed [28] for γ and the molar mass of Cd is 112.41 g mol^{-1}. Fig. 2c depicts the comparison of the computed EQCM frequency shifts with the experimental data of [19] and a satisfactory agreement is noticed.

The foregoing analysis has provided a framework whereby EQCM responses can be deduced from the corresponding cyclic voltammograms. As illustrative examples, UPD systems of Cd and Tl on polycrystalline Ag electrodes were considered. On the other hand, several recent investigations have focused attention on the effect of anions, which bring about morphological changes in UPD phenomena [7]. Analysis of these systems are carried out using EQCM in conjunction with scanning tunnelling microscopy (STM) and ultrahigh vacuum (UHV) techniques. Consequently, a mapping between EQCM response and cyclic voltammograms may be valuable in providing more insights. At the present stage of analysis, these two parameters, i.e., roughness factors and electrosorption valencies [29] were chosen from existing

experimental studies, with plausible justification. A more rigorous approach consists of deducing these values with the help of suitable optimization techniques from the experimental cyclic voltammograms.

Summary

The computation of the EQCM response from the experimental cyclic voltammograms has been demonstrated for two UPD systems, i.e., Cd and Tl on polycrystalline Ag electrodes. A satisfactory agreement between the estimated EQCM frequency shifts and the experimental data is noticed.

References

1. Varineau PT, Buttry DA (1987) J Phys Chem 91:1292
2. Bruckenstein S, Robert Hillman A (1998) J Phys Chem B 102:10826
3. Baek Y, Frankel GS (2003) J Electrochem Soc 150:B1
4. Kutner W, Noworyta K, Marczak R, D'Souza F (2002) Electrochim Acta 47:2371
5. Ebara Y, Okahata Y (1994) J Am Chem Soc 116:1209
6. Deakin MR, Melroy O (1988) J Electroanal Chem 239:321
7. Lay MD, Varazo K, Srisook N, Stickney JL (2003) J Electroanal Chem 221:554–555
8. Buttry DA, Ward MD (1992) Chem Rev 92:1335
9. Schumacher R (1990) Angew Chem Int Ed Engl 29:329
10. In order to obtain accurate estimates of the charge densities for the entire potential window of the cyclic voltammogram, the current density was noted at an interval of 2.5 s
11. Bard AJ, Faulkner LR (1980) Electrochemical methods,chap. 6. Wiley, New York
12. Motheo AJ, Machado SAS, Van Kampen MH, Santos JR Jr (1993) J Braz Chem Soc 4:122
13. Rama Kant (1993) Using the current transients, the structure factor of one and two—dimensional rough surfaces can be deduced as an inverse problem. Phys Rev Lett 70:4094
14. Saurbrey G (1959) Z Phys .155:206 Among various equations describing the relationship between the resonant frequency of an oscillating piezoelectric crystal and the mass deposited, Saurbrey equation is the most widely accepted. However, similar equations have been derived by Stockridge (Stockbridge CD (1966) Vac Microbalance Tech 5:193) and Lostis (Lostis M (1958) PhD Faculty of Science, University of Paris)
15. Zhang J, Sung YE, Rikvold PA (1996) J Chem Phys 104:5699
16. Blum L, Huckaby DA, Legault M (1996) Electrochim Acta 41:2207
17. See for example: Huckaby DA, Blum L (1994) Diffusion processes: experiment, theory, simulations. In Pekalski A (ed) Proceedings of the fifth Max Born symposium, Kudowa, Poland Springer, Berlin Heidalberg New York
18. Schultze JW, Vetter KJ (1973) J Electroanal Chem 44:63
19. Tang Y, Furtak TE (1991) Electrochim Acta 36:1873
20. GIMP is an acronym for the GNU Image Manipulation Program and is a freely available software, capable of functioning under a variety of operarting systems for image authoring and image format conversion. In the present study, GIMP has been employed to obtain accurate numerical estimates of current–potential data from appropriate cyclic voltammograms. These values are then used to obtain the corresponding charge densities
21. Waszczuk P, Wnuk A, Sobkowski J (1996) Electrochim Acta 44:1789
22. Daujotis V, Gaidamauskas E (1998) J Electroanal Chem 446:151
23. Lide DR (ed) (2000) CRC Handbook of chemistry and physics, 80th edn. CRC Press, New York
24. Schumacher R, Borges G, Kanazawa KK (1985) Surf Sci 163:L621
25. Schumacher R, Gordon JG, Melroy O (1987) J Electroanal Chem 216:127
26. Bort H, Juttner K, Lorenz WJ, Staikov G (1983) Electrochim Acta 28:993
27. Jovic VD, Jovic BM (2002) Electrochim Acta 47:1777 (and references therein)
28. The electrosorption valency γ pertaining to the UPD of Cd on Au is reported to vary from 1.6 to 2.0 and γ in the case of the UPD of Cd on Ag is $\approx$ 2.0. A value of 1.7 for γ has been employed in our analysis leading to Fig. 2c. If γ is assumed to be 2.0, an error of ca $\pm 15\%$ is obtained in comparison with experimental data
29. (a) The electrosorption valency (γ) of ions and chemisorbing organic compounds is a measure of the extent of partial charge transfer of the adsorbate with the electrode surface. Within a statistical mechanical framework, the estimation of γ requires suitable adsorption isotherms and models for interfacial potential distribution (Schultze JW, Koppitz FD (1976) Electrochim Acta 21:327). Alternately, quantum mechanical calculations as well as Monte Carlo simulations pertaining to simple halide ions do exist (see for example: Abou Hamad I, Wandlowski Th, Brown G, Rikvold PA(2003) J Electroanal Chem 211:554–555) (b) It is interesting to enquire whether employing the roughness factor and electrosorption valency from the experimental data is appropriate in deducing EQCM response from the CV data while employing Eqs. 8 and 9. However, the roughness factor of any electrode can directly be obtained by estimating the oxide formation on the surface. Analogously, the electrosorption valency of depositing species can be deduced from suitable adsorption isotherms
30. The experimental data of Figs. 1 and 2 were reproduced with permission from Elsevier Science Publishers