ORIGINAL PAPER

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Thermodynamic issues associated with combined cyclic voltammetry and wafer curvature measurements in electrolytes

Abstract A thermodynamic framework has been provided for the interpretation of combined cyclic voltammetry and surface stress measurements, the latter being obtained from wafer curvature or beam deflection measurements of a solid electrode as a function of applied potential (so-called voltstressograms). Firstly, the derivation of electrocapillarity equations for solid electrodes has been critically reviewed by starting from the Gibbs adsorption equation appropriate for solid–electrolyte interfaces. This allowed us to demonstrate the critical importance of elastic surface strain in the thermodynamic boundary conditions of the partial derivatives intervening in the interpretation of voltstressograms. From these considerations, it was shown for the first time that the electrocapillarity equations for solid electrodes are not appropriate for describing the variation of surface stress with potential obtained from wafer curvature measurements, because such measurements are intrinsically incompatible with the constant strain condition implied in the electrocapillarity equations. An alternative explanation is provided for the experimentally observed proportionality between the current density, measured in cyclic voltammograms, and the first derivative of surface stress with respect to potential, obtained from voltstressograms.

Keywords Surface stress · Wafer curvature · Gibbs adsorption equation

Introduction

This paper deals with the interpretation of combined cyclic voltammetry and so-called wafer curvature or

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beam deflection measurements of solid electrodes. In such experiments, the electrode, in the form of a thin sheet or a cantilever, bends elastically in response to an applied variation in potential [1]. This bending, which for typical potential scans and electrode geometries can give rise to an elastic strain at the electrode surface on the order of 10^{-4} [2], is measured with high-resolution optical or capacitive techniques as a change in curvature of the solid electrode. The curvature change is then transformed into a surface stress variation with potential, based on appropriate mechanical constitutive equations [3]. The main interest of such experiments lies in the fact that the surface stress evolution can often be linked to adsorbate-induced modifications of the bond strength in the topmost electrode layer [4, 5]. Since in electrolytes, these adsorbate-induced changes of the surface stress are generally accompanied by charge-transfer effects, the combination of quantitative surface stress measurements with cyclic voltammetry provides a powerful electroanalytical tool for the fundamental understanding of electrode–electrolyte interactions [6, 7].

The issue of surface stress has a long history in electrochemistry, and can be described thermodynamically by the theory of electrocapillarity. The latter name originates from the earliest measurements of the dependence of the surface energy of a liquid mercury electrode on the applied potential [8]. Since for an interface between two liquid media the surface stress is identical to the surface energy, the following relation can be derived between the electrode potential E, the surface charge density σ and the surface energy γ for a liquid electrode [9]:

$$\left(\frac{\partial \gamma}{\partial E}\right)_{T,\mu_i} = -\sigma. \tag{1}$$

This relation, which is strictly valid at constant temperature T and chemical potential μ_i for all species i, is well known as the classical Lippmann equation for liquid–liquid electrochemical interfaces. Note that the quantity γ is often also referred to as the surface *tension*.

As this nomenclature may cause confusion with the surface *stress* g, we have used the term surface energy throughout the current manuscript.

The concepts mentioned above have no bearing on solid electrodes, because the surface stress g of a solid differs from its surface energy γ [10]. The electrocapillarity equation of an elastically stretched solid electrode surface is to be described by the following, modified Lippmann equation [11]:

$$\left(\frac{\partial \gamma}{\partial E}\right)_{T,\mu_i} = -\sigma + (g - \gamma)\left(\frac{\partial \varepsilon_e}{\partial E}\right)_{T,\mu_i}, \qquad (2)$$

ε_e being the elastic surface strain. Over the years, there has been significant confusion in the literature concerning the proper use and interpretation of this equation [12–15]. Of particular interest for this paper is its applicability in combination with electroanalytical experiments, specifically with cyclic voltammograms. To the best of our knowledge, an as yet unclarified apparent inconsistency still persists in the literature, where experiments point to a correlation between the measured current density j and the first derivative $\partial g/\partial E$ [16], while, similar to the well-established case of liquid metal electrodes [17], a correlation with the second derivative $\partial^2 g/\partial E^2$ has been claimed on thermodynamic grounds [6, 13]. It is the aim of the present work to address these inconsistencies. In order to provide the relevant thermodynamic framework, we first come back to the definitions of surface stress and surface energy. We then review the derivation of the electrocapillarity equation (Eq. 2) for solid electrodes by starting from the Gibbs adsorption equation appropriate for solid–electrolyte interfaces. This thermodynamic background will allow us to demonstrate, in the discussion in Sect. 3, the critical importance of elastic surface strain in the thermodynamic boundary conditions of the partial derivatives intervening in the interpretation of voltstressograms. It will be shown for the first time that the electrocapillarity equations for solid electrodes are not appropriate for describing the variation of surface stress with applied potential obtained from wafer curvature measurements, because such measurements are intrinsically incompatible with the constant strain condition implied in the electrocapillarity equations. Finally, an alternative explanation will be presented for the experimentally observed proportionality between the current density, measured in cyclic voltammograms, and the first derivative of surface stress with respect to potential, obtained from voltstressograms.

Thermodynamic background

Surface stress and surface energy

The surface energy γ is defined as the reversible work to form a unit area of new surface by adding or exposing atoms at the equilibrium interatomic spacing, i.e. at constant strain. The surface stress g is associated with the reversible work required to elastically deform a pre-existing surface. In this process, surface area is altered by changing the density of atoms at the surface. When a liquid surface is stretched, new atoms or molecules will arrive at the surface to accommodate the new area created, so that the time-averaged number of atoms per unit area remains constant. As a result, a liquid surface is not able to sustain a surface strain, and the surface energy for a liquid is equal to the surface stress.

Upon elastically stretching a solid surface on the other hand, the number of atoms per unit surface area is altered and therefore $g \neq \gamma$. While the surface stress of a solid is in general to be considered a tensor g_{ij}, for a surface possessing a threefold or higher rotation symmetry, which is the situation of interest throughout this paper, g_{ij} is isotropic and can be taken as a scalar. In that case, the following relationship exists between the surface stress and the surface energy of a solid, known as the Shuttleworth equation [18]:

$$g = \gamma + \frac{\partial \gamma}{\partial \varepsilon_e}. \qquad (3)$$

For most solids, g is of the same order of magnitude as γ, and can be positive or negative. Note that since liquids are not able to sustain elastic stresses at their surface, the second term in Eq. 3 vanishes and $g = \gamma$.

Electrocapillarity equations of solid electrodes

In order to arrive at the electrocapillarity equation for solid electrodes, Couchman and Davidson started from the Gibbs adsorption equation appropriate for plane solid–electrolyte interfaces [19]:

$$d\gamma = -s dT - \sigma dE + (g - \gamma)d\varepsilon_e - \sum_i \Gamma_i d\mu_i, \qquad (4)$$

where T is the absolute temperature, ε_e the elastic surface strain, μ_i the chemical potential of species i, and s, Γ_i and σ denote entropy, surface excesses of species i per unit area and surface charge, respectively. At fixed T and μ_i, this results in :

$$\left(\frac{\partial \gamma}{\partial E}\right)_{T,\mu_i} = -\sigma + (g - \gamma)\left(\frac{\partial \varepsilon_e}{\partial E}\right)_{T,\mu_i} \qquad (5)$$

which is the well-known electrocapillarity equation for an elastically stretched solid electrode, already presented above, see Eq. 2. It describes how the solid–electrolyte interfacial energy γ changes with electrode potential at constant temperature and composition, assuming ideally polarized electrode behaviour. It can be noted that Guidelli has claimed Eq. 4 to be generally valid for any surface deformation ε, rather than for its elastic contribution ε_e only [20]. As we are only considering elastic bending strains throughout the current manuscript, this generalization is not relevant for the current discussion.

The importance of the Gibbs adsorption equation (Eq. 4) as a starting point for the further discussion of this paper lies in the fact that it suggests that $d\gamma$ is an exact differential. Although this statement was not proven explicitly in the work by Couchman and Davidson, indirect experimental proof suggesting that Eq. 4 is indeed an exact differential under the restrictions of an ideally polarizable, elastically strained electrode has recently been provided [21]. In that case, the exact differential can, at fixed T and μ_i, also be written as follows:

$$d\gamma = \left(\frac{\partial\gamma}{\partial E}\right)_{\varepsilon_e} dE + \left(\frac{\partial\gamma}{\partial\varepsilon_e}\right)_E d\varepsilon_e. \tag{6}$$

Consequently, the following expressions for the partial derivatives are obtained after comparison with Eq. 4 [21]:

$$\left(\frac{\partial\gamma}{\partial\varepsilon_e}\right)_{T,\mu_i,E} = g - \gamma, \tag{7}$$

$$\left(\frac{\partial\gamma}{\partial E}\right)_{T,\mu_i,\varepsilon_e} = -\sigma. \tag{8}$$

The first equality retrieves, in essence, the Shuttleworth equation (Eq. 3) for an electrified, isotropic solid surface. However, as compared to the original derivation [10, 18], it now explicitly specifies the hitherto hidden assumption of constant potential. The second equality (Eq. 8) explicitly specifies the critical assumption of constant elastic surface strain. As a result, it is fully consistent with the standard Lippmann equation (Eq. 1) for liquid electrodes, as liquid surfaces, unlike solid ones, are not able to sustain an elastic surface strain.

Finally, as the experimentally observed relation between voltstressograms and voltammograms involves the first derivative of g with respect to E, we close this section by presenting an expression for $\partial g/\partial E$. It is based on Maxwell-type relations involving the second mixed partial derivatives of the exact differential in Eq. 6 [21]:

$$\frac{\partial}{\partial\varepsilon_e}\left[\left(\frac{\partial\gamma}{\partial E}\right)_{\varepsilon_e}\right]_E = \frac{\partial}{\partial E}\left[\left(\frac{\partial\gamma}{\partial\varepsilon_e}\right)_E\right]_{\varepsilon_e}. \tag{9}$$

Substituting, always at constant T and μ_i, the quantities between square brackets with Eqs. 8 and 7 respectively, one obtains the following equations:

$$-\left(\frac{\partial\sigma}{\partial\varepsilon_e}\right)_E = \left(\frac{\partial g}{\partial E}\right)_{\varepsilon_e} - \left(\frac{\partial\gamma}{\partial E}\right)_{\varepsilon_e} = \left(\frac{\partial g}{\partial E}\right)_{\varepsilon_e} + \sigma \tag{10}$$

or

$$\left(\frac{\partial g}{\partial E}\right)_{\varepsilon_e} = -\sigma - \left(\frac{\partial\sigma}{\partial\varepsilon_e}\right)_E. \tag{11}$$

This relation was obtained independently by Gokhshtein as well [22]. Note how it explicitly indicates the implied thermodynamic constraints of, respectively, constant elastic strain and potential for the partial derivatives involved.

Discussion

On the improper use of the electrocapillarity equations

In an effort to correlate the features of cyclic voltammograms to either the first or second derivative of the surface stress with respect to potential, Haiss et al. [13, 16] started by differentiating the Shuttleworth equation (Eq. 3), $g = \gamma + \partial\gamma/\partial\varepsilon_e$ with respect to E, to obtain, after substitution with Eq. 8, the following expression for the first derivative:

$$\frac{\partial g}{\partial E} = -\sigma - \frac{\partial\sigma}{\partial\varepsilon_e}. \tag{12}$$

By differentiating this expression with respect to E after neglecting the second term $\partial\sigma/\partial\varepsilon_e$, they then arrived at the following:

$$\frac{\partial^2 g}{\partial E^2} = -\frac{\partial\sigma}{\partial E} = -\frac{j}{\partial E/\partial t}. \tag{13}$$

Hence, for a voltammogram taken at a linear scan rate (constant $\partial E/\partial t$), a correlation of j with the second derivative $\partial^2 g/\partial E^2$ was claimed, based on Eq. 13.

However, a number of arguments allow us to explicitly disprove the thermodynamic grounds on which Eq. 13 has been validated. Firstly, Eq. 12 cannot be obtained by differentiation of the Shuttleworth equation. In fact, a correct differentiation of the Shuttleworth equation would result, at constant T and μ_i, in

$$\frac{\partial g}{\partial E} = \frac{\partial\gamma}{\partial E} + \frac{\partial}{\partial E}\left(\frac{\partial\gamma}{\partial\varepsilon_e}\right). \tag{14}$$

Inserting Eqs. 5 and 3 for the first order differentials on the right-hand side then results in

$$\frac{\partial g}{\partial E} = -\sigma + (g - \gamma)\frac{\partial\varepsilon_e}{\partial E} + \frac{\partial}{\partial E}(g - \gamma) \tag{15}$$

which, after rearrangement, simply retrieves the electrocapillarity equation Eq. 2 for solid electrodes, instead of Eq. 12. It is obviously not surprising that the Shuttleworth relation cannot be an appropriate starting point for obtaining an expression for $\partial g/\partial E$, as both expressions were shown above to result from the same general Gibbs adsorption equation.

The error made in arriving at Eq. 13 from the Shuttleworth equation basically results from neglecting the second term in Eq. 5 or, equivalently, by wrongly using Eq. 8 to obtain an expression for $d\gamma/E$. In this respect, one of the major sources of confusion in the literature has been the following: although, formally, the generalized Lippmann equation (Eq. 5) for solid electrodes reduces to the one for liquid electrodes (Eq. 8) only at

constant elastic strain, in practice, both equations can be used for describing the electrocapillarity behaviour of solids because the last term in Eq. 5 is generally negligible. Its magnitude has been estimated to be on the order of 10^{-8} C/m^2 [14], which is much smaller than the surface charge densities that are generally measured in electroanalytical experiments. However, it is clear that in formal, thermodynamic derivations of electrocapillarity phenomena involving solid electrodes, as the one used by Haiss et al. [16] for wrongly arriving at Eq. 13, it is the generalized Lippmann equation (Eq. 5) that should be used (a small value of a function does not necessarily mean a small value of the function's derivative).

In general, the use of Eq. 8 in any thermodynamic derivation involving the interpretation of wafer curvature measurements of solid electrodes necessarily leads to erroneous results, as per definition, elastic strain is involved during the measured bending of the electrode with applied potential. For the same reason, the condition of constant strain also impedes the use of the Gokhshtein equation (Eq. 11) for the interpretation of voltstressograms, because this condition is again inherently incompatible with wafer curvature or beam deflection experiments. In other words, wafer curvature measurements do not allow to investigate the variation of surface stress with applied potential at constant strain. The above argument stresses the critical importance of correctly specifying the implied thermodynamic boundary conditions in all the partial derivatives intervening in the interpretation of voltstressograms. The lack of such specification is, in our opinion, one of the major reasons for the still-persisting thermodynamic inconsistencies in the literature regarding this subject.

Alternative explanation

From the discussion above, it is clear that an explanation for the relation between voltammograms and voltstressograms should not involve any of the electrocapillarity equations. The correlation between both can, in fact, be understood in a rather straightforward way by considering the contribution of specific adsorption, as originally suggested by Guidelli [20] based on experiments involving the solid–vacuum interface [23, 24]. We develop a similar argument here for the solid–electrolyte interface by starting from a well-established experimental observation, namely the strict proportionality between the current density j measured in cyclic voltammograms, and the first derivative $\partial g / \partial E$ obtained from voltstressograms [16]. This can be expressed as

$$j = K \frac{\mathrm{d}g}{\mathrm{d}E}, \tag{16}$$

K being a proportionality constant with dimensions t^{-1}. Since $j \equiv \mathrm{d}\sigma / \mathrm{d}t$ and $\mathrm{d}E \equiv R \cdot \mathrm{d}t$, R being the constant scanning rate of a linear potential scan, Eq. 16 becomes

$$\frac{\mathrm{d}\sigma}{\mathrm{d}E} = \frac{K}{R} \frac{\mathrm{d}g}{\mathrm{d}E}. \tag{17}$$

Hence, if Eq. 16 is valid, as is indeed observed experimentally, this also implies that during combined voltammetry and wafer curvature experiments the following condition holds:

$$\frac{\mathrm{d}g}{\mathrm{d}\sigma} = \text{constant}. \tag{18}$$

Regarding the latter variation of surface stress g with surface charge density σ, Schmickler and Leiva [24] have pointed out, based on model calculations involving jellium-type and lattice gas models, that it is mainly governed by the response of the metal electrode itself, through the change in the bond charge density at the topmost electrode layer. However, they also concluded that any fine structure that may be observed must be due to adsorption at specific sites, the contribution of adsorbates to g depending strongly on the coverage. In this respect, experimental evidence from the literature has indeed confirmed the validity of Eq. 18, at least in the limit of low coverages, by recording g directly as a function of σ by on-line integration of the current density [16]. In fact, from a theoretical point of view, Schmickler and Leiva have already provided direct proof, based on their model calculations, for the validity of the experimental observation expressed in Eq. 16, at least in the case where the contribution of adsorbates to g can be considered to be linear [24]. Our own argument, outlined above, is fully compatible with their findings, but based on a different starting point, namely an experimentally confirmed and accepted relation (Eq. 18) between two experimentally accessible key parameters (g and σ) of combined voltstressograms and voltammograms.

A final note concerns the cited experimental evidence for the validity of Eq. 18. While in [16] the constancy of $\mathrm{d}g / \mathrm{d}\sigma$ was confirmed for combined voltammetry and wafer curvature experiments, Gokhshtein [22] experimentally assessed the quantity $\mathrm{d}g / \mathrm{d}\sigma$ by so-called estance techniques, and showed it to vary significantly over a relatively small potential range, including several sign changes. His experiments however aimed at confirming the validity of the following thermodynamic relationship:

$$\left(\frac{\partial g}{\partial \sigma} \right)_{\varepsilon_e} = \left(\frac{\partial E}{\partial \varepsilon_e} \right)_{\sigma}, \tag{19}$$

the derivation of which has been discussed in [21]. The estance technique was chosen in this respect because it involves differential surface stress measurements at infinitesimal strains (smaller than 10^{-8}) [26], a prerequisite imposed by the boundary condition of the left-hand side term of Eq. 19. As a result, these measurements have no bearing on the wafer curvature and beam bending experiments considered in [16] and throughout this work, which for typical potential scans

and electrode geometries can give rise to elastic bending strains at the electrode surface on the order of 10^{-4} [2].

Conclusions

We have provided a number of arguments for resolving still persisting apparent thermodynamic inconsistencies in the literature regarding the interpretation of combined cyclic voltammetry and wafer curvature measurements of solid electrodes. In particular, we have shown that

1. The electrocapillarity equations for solid electrodes are not appropriate for describing the variation of surface stress with applied potential obtained from wafer curvature or beam deflection measurements. The major reason is that such measurements are intrinsically incompatible with the constant strain condition implied in the electrocapillarity equations.
2. The experimentally observed proportionality between the current density j measured in cyclic voltammograms, and the first derivative $\partial g / \partial E$ obtained from voltstressograms is a consequence of the linear dependence of surface stress on charge density. The latter results from the well-established experimental observation that, at least in the limit for low coverages, the change in surface stress caused by chemisorption is proportional to the surface concentration of the chemisorbed species.

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