International Journal of Thermophysics, Vol. 27, No. 6, November 2006 (© 2006)
DOI: 10.1007/s10765-006-0117-3

A Microscopic Theory of Current Density Spikes Associated with Phase Transitions on Crystalline Electrodes[1]

I. Medved'[2,3] and D. A. Huckaby[4]

A microscopic theory that can be used to generate voltammogram spikes associated with first-order phase transitions is presented. The theory can be readily applied to experimental voltammogram spikes in order to determine microscopic properties of the phases involved in the associated transitions.

KEY WORDS: first-order phase transition; lattice gas; voltammogram.

1. INTRODUCTION

The deposition of a metal ion on a foreign metal electrode at potentials at which bulk deposition will not occur is called underpotential deposition. If a first-order phase transition occurs on the crystalline electrode surface during the deposition process, it causes the appearance of a sharp spike in the associated voltammogram (the current density versus potential plot). We present a statistical mechanical theory from which such voltammogram spikes as well as the values of interactions in a lattice gas model simulating the deposition process can be obtained.

We start with the observation that the adsorption sites on an electrode surface are contained in a large number of finite "crystalline domains," to be called crystals, that are mutually separated by "zones

---

[1] Paper presented at the Seventeenth European Conference on Thermophysical Properties, September 5–8, 2005, Bratislava, Slovak Republic.

[2] Department of Physics, Constantine the Philosopher University, 94974 Nitra, Slovak Republic.

[3] To whom correspondence should be addressed. E-mail: imedved@ukf.sk

[4] Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, U.S.A.

of defects." Depending on its size, shape, and boundary conditions, each crystal gives a contribution to the overall current density. Therefore, we interpret a voltammogram spike as an averaged result of contributions coming from every crystal. As we pointed out in Ref. 1, it is improper to consider a voltammogram spike as a result of a first-order phase transition in a single crystal: the current density from a "typical" single crystal with several hundred sites exhibits a spike that is hundreds of times taller and sharper than those seen in experiments.

A contribution from a single finite crystal to the overall current density can be described with the help of the rigorous results of Borgs and Kotecký [2] on the finite-size effects near first-order phase transitions. Their results can be applied to a wide class of lattice models and show that, quite generally, the behavior of the current density from a single crystal is strikingly universal, depending only on a few parameters. Thus, we need not use a specific lattice gas model to simulate a phase transition on the electrode surface. It suffices to work only with these few parameters that distinguish the contributions from different crystals.

Nevertheless, if one constructs a lattice gas to model a phase transition during the deposition process, relationships can be obtained between the crystal parameters and the microscopic interactions in the lattice gas model. Experimental features of the voltammogram spike can be used to obtain the crystal parameters from which the microscopic interactions in the model can be calculated. As an illustration, we apply the theory to the underpotential deposition of copper on the (111) surface of a platinum electrode.

2. ELECTRODE CURRENT DENSITY

2.1. The Setting

Assuming that the Faradaic part of the current is due to the discharge of a single type of ion ι, and neglecting any capacitive contributions, the current density at the electrode surface is given as [3]

$$J(\psi) = -\kappa e_0 \gamma \nu \frac{\partial \Theta(\psi)}{\partial \psi}. \tag{1}$$

Here κ is the density of adsorption sites on the electrode, e_0 is the elementary charge, γ is the effective electrovalence of ι, ν is the sweep rate, Θ is the electrode coverage of ι, and ψ is the applied electric potential. We assume that $J(\psi)$ contains a spike corresponding to a first-order transition between two phases on the electrode surface.

2.2. Current Density from a Single Crystal

Let $\Delta\theta$ be the difference of the coverage of the ion ι in the two phases and let $a = \Delta\theta\kappa e_0\gamma\nu$ and $h = a^2/(4\kappa\nu)$. One may introduce a "surface tension" τ such that the single-crystal current density $j(\psi)$ can be very well approximated as [1,2]

$$j(\psi) \approx h\beta S \cosh^{-2}\left[2\,\frac{h\beta S}{a}\,(\psi - \bar{\psi})\right]. \tag{2}$$

Here $\beta = 1/(k_B T)$ is the inverse temperature, S is the number of adsorption sites in the crystal, and

$$\bar{\psi} \approx \psi_t - \frac{\tau a \xi}{4h\sqrt{S}} \tag{3}$$

is the single point at which $j(\psi)$ attains its maximal value (ψ_t is the phase-transition point and $\xi \equiv \frac{\partial S}{\sqrt{S}}$ is a shape function). We see that $j(\psi)$ exhibits a *symmetric* spike of height $\propto S$ and of width $\propto 1/S$ around $\bar{\psi}$. The shift of $\bar{\psi}$ with respect to ψ_t is of order $\partial S/S$ and depends on the "surface tension" τ characterizing the details of the interactions of the crystal with its surroundings (the boundary conditions). On the other hand, the $\cosh^{-2}$ profile of $j(\psi)$ is τ-independent. Notice also that the area $\int j(\psi)\,d\psi \approx a$ of the spike, Eq. (2), is essentially the same for every crystal.

Remark. *The quantity h is the height (i.e., the maximal value) of the current density $j(\psi)$ from a crystal of size $S = 1$ and at the inverse temperature $\beta = 1$. As already pointed out, the quantity a represents the area of the spike exhibited by $j(\psi)$. The "surface tension" τ is, more precisely, the difference of the surface free energy densities corresponding to the two phases involved in the phase transition.*

The approximation, Eq. (2), is valid when β and S are sufficiently large and the boundary conditions are "weak" (τ is relatively close to 0). However, numerical results show [1] that Eq. (2) can be used even for room temperatures and for crystals of linear size of about 5.

2.3. $J(\psi)$ as an Average

Using the idea that a voltammogram spike is a cumulative result of contributions from a large number of crystals on the electrode surface, and assuming that the crystals do not mutually interact, the electrode current density $J(\psi)$ becomes, in view of Eq. (2), a triple average of its crystal contributions $j(\psi)$; i.e. [1,4,5],

$$J(\psi) = \langle \langle \langle j(\psi) \rangle_\xi \rangle_\tau \rangle_S. \tag{4}$$

Since the area a of the spike of $j(\psi)$ is practically the same for every crystal, none of the three averages will change it, and the area $\int J(\psi)\, d\psi$ of $J(\psi)$ is also approximately equal to a.

3. EVALUATION OF $J(\psi)$

In order to demonstrate the evaluation of the electrode current density $J(\psi)$ through Eq. (4), we will use these two technical simplifications:

1. All the crystals will have the same parallelogram shape (this is not a very serious restriction [5]). The dimensionless "shape factor" ξ then has a fixed value, and the corresponding ξ-average in Eq. (4) is vacuous, i.e., $J(\psi) = \langle \langle j(\psi) \rangle_\tau \rangle_S$.
2. We will work with Gaussian probability distributions to evaluate the averages over τ and S. To this end, we define the Gaussian $G(x; w, A) = (A/w)\exp[-\pi(x/w)^2]$. It has an area A, a maximum at the point $x = 0$, a height A/w, and a half-width $w\sqrt{(\log 8/\pi)} \approx 0.94w$.

3.1. The τ-Average

Observing that $\cosh^{-2} x \approx \exp[-\pi(x/2)^2]$, we may approximate the spike, Eq. (2), exhibited by $j(\psi)$ by the Gaussian $G(\psi - \bar{\psi}; w_1, a)$ with $w_1 = a/(h\beta S)$ and thus easily evaluate the average over the "surface tension" τ. We will use $G(\tau - \tau_0; w_\tau, 1)$ for the probability distribution of τ, where τ_0 is the mean value of τ and w_τ is the corresponding half-width. Since τ is a boundary quantity, w_τ is to be of the order $1/\sqrt{\partial S}$ of boundary fluctuations. Recalling that $\xi = \frac{\partial S}{\sqrt{S}}$, we set $w_\tau = 1/[\delta_\tau \sqrt{(\xi\sqrt{S})}]$ with some $\delta_\tau > 0$. Combined together,

$$\langle j(\psi) \rangle_\tau \approx \int G(\psi - \bar{\psi}; w_1, a)\, G(\tau - \tau_0; w_\tau, 1)\, d\tau = G(\psi - \bar{\psi}_0; w_2, a), \tag{5}$$

where $\bar{\psi}_0 = (\bar{\psi})_{\tau = \tau_0}$ and

$$w_2 = \sqrt{w_1^2 - (C_S w_\tau)^2} \approx C_S w_\tau \tag{6}$$

with $C_S = a\xi/(4h\sqrt{S})$. In the last step we noticed that $w_1/(C_S w_\tau) = \delta_\tau/[\beta\sqrt{(\xi\sqrt{S})}] \ll 1$.

The effect of the τ-average is a dramatic decrease in the spike height from $\propto S$ [see Eq. (2)] to $C_S w_\tau \propto S^{3/4}$. Since the area remains intact by the averaging, this also means a corresponding dramatic increase in the width.

3.2. The *S*-Average

In the evaluation of the average over the crystal sizes S, we consider $G(S - S_0; w_S, 1)$ as the probability distribution of S, where S_0 is the mean value of S and w_S represents the half-width. For a proper normalization of the distribution, the restriction $w_S \lesssim S_0$ is necessary. In view of Eqs. (5) and (6), we find

$$J(\psi) \approx J_0(\psi) \equiv \int_0^\infty G(\psi - \bar{\psi}_0; C_S w_\tau, a)\, G(S - S_0; w_S, 1)\, dS. \tag{7}$$

Although the integral $J_0(\psi)$ cannot be evaluated analytically, it may be well approximated by such an integral [4]. Namely, if we approximate w_τ by the S-independent half-width $w_\tau^0 = 1/[\delta_\tau\sqrt{(\xi\sqrt{S_0})}]$, then Eq. (6) is replaced by $w_2 \approx C_S w_\tau^0$. Approximating also w_S by w_{S_0}, the integral $J_0(\psi)$ becomes

$$J_0(\psi) \approx J_1(\psi) \equiv \int_0^\infty G(\psi - \bar{\psi}_0; C_S w_\tau^0, a)\, G(S - S_0; w_{S_0}, 1)\, dS. \tag{8}$$

The integral $J_1(\psi)$ may be evaluated analytically. We do not give its explicit analytic form, however, as it is quite complex. We rather illustrate the result in Fig. 1. The usefulness of $J_1(\psi)$ lies in the fact that its characteristics, considered in the next section, can be much easier analyzed than those of $J_0(\psi)$ [5]. One may always check numerically if the approximation $J_1(\psi)$ of $J_0(\psi)$ is appropriate (see Fig. 1).

4. FITTING $J(\psi)$ TO EXPERIMENT

When fitting the theoretical electrode current density $J(\psi)$ to an experimental voltammogram spike, one chooses a few characteristics of the spike that can be both simply measured and estimated from the theory. Their values taken from experiment then determine the function $J(\psi)$. We choose these four characteristics: the area $A = \int J(\psi)\, d\psi$, the maximum position $\psi_{\max}$ of the spike, the height $J(\psi_{\max})$, and an asymmetry factor $\alpha = (\int_{-\infty}^{\psi_{\max}} J(\psi)\, d\psi)/A$ (the ratio of the spike area to the left of the maximum and the total area).

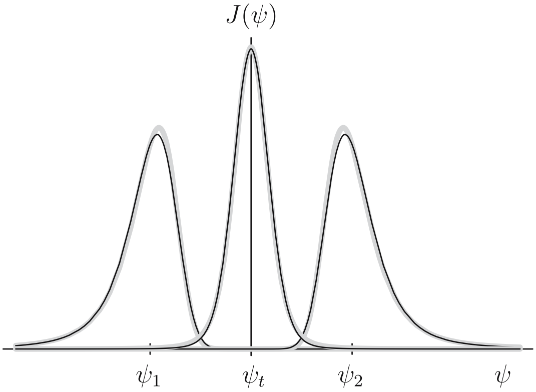

Fig. 1. The current density $J_0(\psi)$ (gray lines) compared to the approximation $J_1(\psi)$ (black lines) for $\tau_0 = 0$ (the two symmetric spikes in the center), $\tau_0 > 0$ (on the left), and $\tau_0 < 0$ (on the right). Symmetric spikes have maxima at ψ_t, the maxima of asymmetric spikes are very close to $\psi_1 = (\bar{\psi})_{\tau=\tau_0}$ and $\psi_2 = (\bar{\psi})_{\tau=-\tau_0}$. Notice that the change of the sign of τ_0 reflects the current densities around ψ_t.

As an example of this idea, we consider the voltammogram spike that results from the first-order phase transition that occurs as an ion ι adsorbs and discharges to form a commensurate monolayer ($\Delta\theta = 1$) on the electrode surface. For the specific case of the underpotential deposition of Cu on Pt(111) (see Fig. 3a in Ref. 6), the values of the four characteristics of the experimental spike are $A = 0.478\ \mu\text{A·V·cm}^{-2}$, $\psi_{\max} = 0.346$ V, $H = 23.348\ \mu\text{A·cm}^{-2}$, and $\alpha = 0.5$ (the voltammogram spike is almost symmetric) [1]. The corresponding scan rate $\nu = 1.0\,\text{mV·s}^{-1}$.

From the relations between A, $\psi_{\max}$, H, and α and the parameters of the theory, the values of four theoretical parameters (γ, ψ_t, τ_0, and δ_τ) can be obtained, whereas the values of the remaining parameters appearing in the theory (ξ, S_0, and w_{S_0}) must be plausibly chosen. We obtain $\gamma = 1.981$, $\psi_t = \psi_{\max} = 0.346$ V, $\tau_0 = 0\,\text{eV}$, and $\delta_\tau = 0.98\,\text{eV}^{-1}$ for $\xi = 4\sqrt{(2/\sqrt{3})} \approx 4.3$ (adsorption sites on the (111) electrode surface form a triangular lattice), $S_0 = 180$ (i.e., the linear size of the crystal is $\sqrt{180} \approx 13.4$), and $w_{S_0} = S_0$. In Fig. 2 we show the comparison of the theoretical and experimental voltammograms. A very good match is obtained.

If a microscopic statistical mechanical lattice gas is constructed to model the first-order phase transition, the four experimental characteristics of the corresponding voltammogram spike can also be used to calculate the strengths of the interaction energies in the model. The phase transition

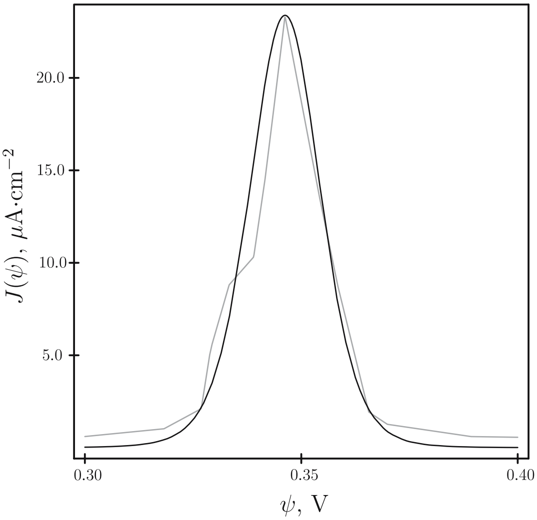

Fig. 2. The experimental voltammogram spike of the underpotential deposition of Cu on Pt(111) from [6], Fig. 3a (gray line), compared to the theoretical electrode current density $J_0(\psi)$ (black line). Pictured is the voltammogram spike that occurs during the stripping process, with a scan rate of $\nu = 1.0\,\text{mV·s}^{-1}$.

to a monolayer, that occurs during the underpotential deposition of Cu on Pt (111), can be modeled by a one-component lattice gas on a triangular lattice with a sufficiently strong nearest-neighbor attraction $\epsilon < 0$ (see Ref. 1 and the references therein). The interaction with a physically suitable fixed boundary is limited to nearest neighbors of the crystal and has a strength $\omega < 0$ that varies from crystal to crystal, its average being equivalent to the average over the "surface tension" τ in Eq. (4). In fact, $\tau_0 = 2\omega_0 - \epsilon$ [1] (ω_0 is the mean value of ω) and $\delta_\tau = 1/[2(\sqrt{\ln 4})|\epsilon|]$ [4]. The above values of τ_0 and δ_τ yield $\epsilon = -433.4\,\text{meV}$ and $\omega_0 = \epsilon/2 = -216.7\,\text{meV}$ [1].

In addition to its use for symmetric voltammogram spikes, like the example in Fig. 2, our theory, based on Eq. (4), can also be used for experiments with asymmetric spikes. The symmetric situation is a very special case, corresponding to $\tau_0 = 0$ (see Fig. 1). For all cases in which $\tau_0 \neq 0$, the corresponding current density spike is asymmetric. Our statistical mechanical theory, generalized to treat asymmetric voltammogram spikes, will appear in Ref. 5.

5. CONCLUDING REMARKS

There may be several factors determining the broadening and asymmetry of voltammogram spikes occurring due to first-order phase transitions. In this article we presented a *quasi-equilibrium* (low potential scan rate) theory based on the hypothesis that voltammogram spikes are results of the finite-size effects (at first-order phase transitions) in variously sized crystalline domains formed on the electrode surface. In many experiments, however, especially with higher potential scan rates, a significant hysteresis takes place, resulting in relative displacement of the positive-going stripping and the negative-going deposition peaks. In such situations kinetic effects may be important for spikes' broadening and displacement (see the results of Monte Carlo simulations from Refs. 7 and 8). In the present study we considered only the stripping peaks for which kinetic effects should be less important than for the deposition peaks.

ACKNOWLEDGMENTS

This research was supported by the Robert A. Welch Foundation, Grant P-0446, and by Grant VEGA 1/3031/06 and Grant CGA V/4/2005. I.M. would like to thank D.A.H. and express his appreciation for the hospitality extended to him during his stays at TCU.

REFERENCES

1. D. A. Huckaby and I. Medved', *J. Chem. Phys.* **117**:2914 (2002).
2. C. Borgs and R. Kotecký, *J. Stat. Phys.* **79**:43 (1995).
3. L. Blum and D. A. Huckaby, *J. Electroanal. Chem.* **375**:69 (1994).
4. I. Medved' and D. A. Huckaby, *J. Chem. Phys.* **118**:11147 (2003).
5. I. Medved' and D. A. Huckaby, *J. Stat. Phys.* (in press).
6. J. H. White and H. D. Abruña, *J. Chem. Phys.* **94**:894 (1990).
7. G. Brown, P. A. Rikvold, S. J. Mitchell, and M. A. Novotny, in *Interfacial Electrochemistry: Theory, Experiment, and Applications*, A. Wieckowski, ed. (Marcel Dekker, New York, 1999), pp. 47–61.
8. P. A. Rikvold, G. Brown, and S. J. Mitchell, in *Encyclopedia of Surface and Colloid Science*, A. Hubbard, ed. (Marcel Dekker, New York, 2002), pp. 4814–4824.