PHYSICAL REVIEW E **68**, 051502 (2003)

Nonlinear voltage profiles and violation of local electroneutrality in ordinary surface reactions

Wayne M. Saslow
Department of Physics, Texas A&M University, College Station, Texas 77843-4242, USA

(Received 9 April 2003; published 7 November 2003)

It is normally assumed that ordinary surface reactions, which involve no charge transfer between the surface and electrolyte, have no effect on voltage. The present work shows, on the contrary, that nontrivial voltage profiles *can* be produced by ordinary surface reactions. Poisson's equation then implies a nonzero bulk charge density, so that local electroneutrality is violated. The specific system considered is a planar lead-acid cell, but the results apply more generally, so long as the electrolyte charge-carrier diffusivities are not all the same. For slow steady reactions the carrier fluxes vary linearly across the cell, which produce linearly varying electric field and density gradients. As a consequence the voltage profile varies quadratically, and the volume charge density is nonzero and uniform. This result has broad implications (e.g., to steady-state oxygen loading of high T_c materials) and may provide a contributing mechanism for the origin of the electric fields observed during biological growth.

DOI: 10.1103/PhysRevE.68.051502 PACS number(s): 82.45.Tv, 82.45.Gj, 05.70.Ln, 66.10.−x

I. INTRODUCTION

It is well known that slow and steady reactions involving charge transfer between electrode and electrolyte produce a voltage profile across the electrolyte (either a solid, such as the high T_c superconductor La_2CuO_{4+x}, or a fluid, such as H_2SO_4). However, only recently was it shown that, when the transport equations are linearized in the current amplitude (in practice, this means taking uniform ionic conductivities), the resulting voltage profile can be spatially nonlinear. Such spatially nonlinear profiles occur for both fluid and solid electrolytes [1,2]. As a consequence, the frequently assumed "principle" of local electroneutrality is violated [1], and resistances measured by Ohmic means ($R_{ohm}=\Delta V/I$) and by Joule heating ($R_{joule}=\mathcal{P}_{heat}/I^2$) can differ [3].

Specifically, solution of the transport equations (including Gauss's Law) in the limit of small ion flux yields that during slow, steady charging (or discharging) the voltage profile across a planar lead-acid cell varies quadratically in space [1]. For such slow steady surface reactions at the Pb and PbO_2 electrodes, nonconvective ionic fluxes of hydrogen (H^+) and sulfate (HSO_4^-) in the bulk can keep up with the ionic demands of the surface reactions, so that the rate of ionic depletion (or accretion) is uniform in the cell volume. The continuity equation in one dimension then implies that the ion fluxes have a constant slope—implying that they vary linearly across the cell. Gauss's Law and the Planck-Nernst equations for ionic migration and diffusion then imply that the other vectors in the problem—the electric field and the ionic density gradients—also vary linearly in space. The equations further imply that the voltage profile varies quadratically in space, and that the bulk charge density is a nonzero constant [1]. In the present work we apply the same approach to the lead-acid cell on open circuit, but including the inevitable self-discharge reactions that cause batteries to "go bad" when not regularly recharged. Because these reactions demand ion fluxes to the electrodes, we again find a quadratic voltage profile, despite the absence of electric current flow, although the details differ from the profiles for charge and discharge.

The method employed in Ref. [1] to study the electrolyte of the lead-acid cell was called the "principle of uniform depletion." The origin of this name is that, for slow steady discharge of a lead-acid cell, drift and diffusion within the bulk can keep up with the demands of the reactions at the electrode-electrolyte interface, and thus the bulk concentration decreases nearly uniformly in time. (There is, however, a small concentration gradient proportional to the current.) An analogy was made to a slowly emptying bathtub, wherein the water level in the tub decreases nearly uniformly despite the fact that the tub empties at only one end. To verify this analogy supporting a uniform rate of depletion, the small amplitude frequency response of this system was studied; as noted in the penultimate paragraph of Ref. [1], in the limit of low frequencies the two solutions agreed. What could be called a "principle of uniform expansion and compression" is implicit in Helmholtz's studies of low frequency acoustic resonances [4]. This principle has been employed in a study of superfluid flow in packed powders, where for a one-dimensional geometry open at one end it yields a velocity profile that is linear in space [5].

For currents large enough to cause 50% deviations from equilibrium ion densities, Newman has assumed local electroneutrality and then estimated that the extent of its violation is very small [6]. No assumption of local electroneutrality is made in Chazalviel's work on electrodeposition and electrodissolution of metal electrodes and dilute salt solutions containing cations of the metal [7]. This, unlike the present work, considers nonlinear effects. Given the present ease of numerical computation, it is no longer necessary to simplify the transport equations in order to solve them, and progressively more work does not assume local electroneutrality. For violations of local electroneutrality in semiconductors, see Refs. [8] and [9].

Using a current density of 10^{-2} A/cm^2 and plate separation $d=1$ mm, Ref. [1] predicts a volume charge density of about 2.5×10^{-12} C/cm^3. (Global electroneutrality is maintained by charge located within a Debye length of the electrodes.) The corresponding fractional change in ionic density is less than 10^{-14}. On the other hand, in the voltage profile the quadratic and linear variations are predicted to be comparable. The only technical requirement for a significant component of quadratic variation in the voltage profile is that the ion diffusivities must differ significantly; otherwise diffusion alone would be able to satisfy the demands of the reactions at the electrode surfaces. Since H^+ ions have about seven times the diffusion constant of $HSO_4{}^-$ ions, this requirement is well satisfied in the lead-acid cell.

Such a quadratic voltage profile for slow, steady surface reactions involving charge transfer should be the rule rather than the exception, so long as the ion diffusivities differ. Indeed, Ref. [2] studied electrical transport by La_2CuO_{4+x} and La_2NiO_{4+x}, solid electrolytes that are mixed ionic, electronic conductors. In these systems the charge carriers are O^{2-} and holes, with very different diffusivities. Rods of these materials are predicted to develop a quadratic voltage profile during slow, steady electrochemical oxygenation wherein O^{2-} "loads" at one end and electrons leave at the other end.

Properly speaking, such surface reactions, involving charge transfer between electrode and electrolyte (called *faradaic reactions*), lie within the province of electrochemistry. On the other hand, the present work considers ordinary surface reactions, which involve *no* charge transfer between electrode and electrolyte (and thus called *nonfaradaic* reactions). However unexpected a quadratic voltage profile is for slow, steady faradaic reactions, the present work reports an even more unexpected result: slow, steady nonfaradaic surface reactions also produce a quadratic voltage profile. This actually constitutes two results: (1) nonfaradaic surface reactions produce a nontrivial voltage profile; (2) this voltage profile varies quadratically in space, and thus local electroneutrality does not hold. It is essential that the ion diffusivities be different.

We consider the specific case of a planar lead-acid cell (so that our results apply to the voltaic cells of a battery sitting on a shelf or in a car that is not being used). It is well known that nonfaradaic surface reactions cause such a battery to discharge; the present work implies that such discharge can be monitored by the voltage profile within the electrolyte. From a practical viewpoint, since for a lead-acid cell the self-discharge rate depends on the characteristic pore size within the electrode (faster for more open pores and slower for more closed pores, in proportion to the reaction area of the electrodes), such discharge must decrease slowly with time [10–12]. When a battery discharges or charges via faradaic reactions, unless the rates are extreme the faradaic and nonfaradaic surface reactions are independent. Hence studies of the voltage profile due to faradaic reactions alone must, in real systems, also include the effect of nonfaradaic surface reactions. During charge or discharge the faradaic reactions dominate, but otherwise the nonfaradaic surface reactions (which are always present) are the only ones to occur.

The present work implies that, if one or both ends of a rod of La_2CuO_{4+x} are subjected to a high pressure of gaseous oxygen (as is often done to change the stoichiometry), so that by an ordinary surface reaction O^{2-} and holes enter the rod, thus "charging" the rod, then a voltage profile will develop across the rod. Correspondingly, if a rod that has been "overcharged" with oxygen is subjected to a vacuum at both ends, so that the rod tends to lose oxygen, then a voltage profile with the opposite slope will develop across the rod.

Section II summarizes Ref. [1], which analyzed a one-dimensional cell containing concentrated H_2SO_4 in terms of the faradaic reactions of H^+ and $HSO_4{}^-$ ions at the Pb and PbO_2 electrodes of a lead-acid cell. Section III shows how slow, steady nonfaradaic surface reactions that are constant in time produce a quadratic voltage profile. Section IV concludes with a discussion of how this effect might be measured, and of its biological implications.

II. FARADAIC REACTIONS

Let H refer to H^+ ions and S refer to $HSO_4{}^-$ ions, with ionic number densities n_H and n_S, and ionic fluxes j_H and j_S. Reference [1] considers a one-dimensional cell containing concentrated sulfuric acid, with active ions H^+ and $HSO_4{}^-$. (For cylindrical and spherical geometries, see Ref. [13].) Following Ref. [1], the Pb electrode is at $x=0$ and the PbO_2 at $x=d$. At the Pb electrode the faradaic reaction is taken to be [10,11]

$$\mathrm{Pb}+\mathrm{HSO_4}^- \rightarrow \mathrm{PbSO_4}+\mathrm{H}^+ + 2e^-. \tag{1}$$

At the PbO_2 electrode the faradaic reaction is taken to be

$$\mathrm{PbO_2}+3\mathrm{H}^+ + \mathrm{HSO_4}^- + 2e^- \rightarrow 2\mathrm{H_2O}+\mathrm{PbSO_4}. \tag{2}$$

Clearly, during discharge the added e's make Pb the negative electrode and the removed e's make the PbO_2 the positive electrode. These reactions cause equal depletion rates of H^+ and $HSO_4{}^-$ when averaged over the two electrodes. For slow, steady reactions this statement implies uniform and equal depletion rates for each ionic species; thus $\partial_t n_H = \partial_t n_S$ is a constant in space.

The continuity equations for the ionic densities n and for the ionic fluxes are

$$0=\partial_t n_H + \partial_x j_H, \quad 0=\partial_t n_S + \partial_x j_S. \tag{3}$$

For slow, steady reactions these equations lead to ionic fluxes having the same slope. Applying the boundary conditions determined by (1) and (2), the bulk fluxes are given by

$$j_S(x)=j_0\left(-1+2\frac{x}{d}\right), \quad j_H(x)=j_0\left(1+2\frac{x}{d}\right). \tag{4}$$

Here $j_0>0$ corresponds to discharge. From Eq. (3), the electric current density J is, with e the magnitude of the electron charge,

$$\begin{aligned} J(x) &= -ej_S(x)+ej_H(x)=ej_0\left(1-2\frac{x}{d}\right)+ej_0\left(1+2\frac{x}{d}\right) \\ &= 2ej_0. \end{aligned} \tag{5}$$

Thus the current I is given, for a cell of cross-sectional area A, by

$$I=JA=2ej_0A. \tag{6}$$

Note that $I>0$ for $j_0>0$ (discharging), and $I<0$ for $j_0<0$ (charging). A characteristic steady value for I is 200 mA, which, with a plate area A of $100\ \mathrm{cm}^2$, gives $ej_0=10\ \mathrm{A/m}^2$. The characteristic time to reach steady state is [14]

$$\tau=\frac{d}{\pi}{}^{2}\frac{1}{\tilde{D}}, \quad \tilde{D}=\frac{2D_HD_S}{D_H+D_S}. \tag{7}$$

For $d=1$ mm and $D_S=1.3\times10^{-9}\ \mathrm{m}^2/\mathrm{s}$, $D_H=9.3\times10^{-9}\ \mathrm{m}^2/\mathrm{s}$, so $D_H\approx7D_S$, which gives $\tau=40$ s. Since the decay is exponential, after $t=2.5\tau=100$ s the steady state is effectively attained. In this case, the amount of charge per unit area that enters or leaves the system is of the order of $2ej_0\tau$, which corresponds to number-density changes of $\delta n=2j_0\tau/d$. For the present case, with $ej_0=10\ \mathrm{A/m}^2$, $d=1$ mm, and $\tau=40$ s, the result is $\delta n=5.0\times10^{24}/\mathrm{m}^3$.

The system also satisfies Gauss's law, which relates the divergence of the electric field $\vec{E}$ to the local charge density ρ. Writing E for E_x, and with charge density $\rho=e(n_H-n_S)$, Gauss's law in one dimension is

$$\frac{\partial E}{\partial x}=\frac{\rho}{\epsilon}=\frac{e}{\epsilon}(n_H-n_S). \tag{8}$$

Here $\epsilon=\kappa\epsilon_0$, $\kappa\approx78$ for water, and ϵ_0 is the permittivity of free space.

Finally, since we neglect convection, the ionic fluxes are driven both by migration due to E and by diffusion due to concentration gradients. This fact is contained in the Planck-Nernst equations

$$ej_H=\sigma_HE-eD_H\frac{\partial n_H}{\partial x}, \tag{9}$$

$$-ej_S=\sigma_SE+eD_S\frac{\partial n_S}{\partial x}, \tag{10}$$

where D_H and D_S are diffusivities and σ_S and σ_H are conductivities, related by the Einstein relations

$$\frac{\sigma_{H,S}}{D_{H,S}}=\frac{e^2n_{H,S}}{k_BT}. \tag{11}$$

To solve these equations, we first take the gradient of both sides of Eq. (8), and then use Eqs. (9) and (10) to eliminate the density gradients. This gives

$$\frac{\partial^2E}{\partial x^2}=\frac{e}{\epsilon}\left[\left(\frac{\sigma_H}{D_H}+\frac{\sigma_S}{D_S}\right)\frac{E}{e}-\left(\frac{j_H}{D_H}-\frac{j_S}{D_S}\right)\right]. \tag{12}$$

Since Eq. (4) shows that j_H and j_S are linear in x, it is consistent to take $E=E_x$ to be linear in x, since then the left-hand side of Eq. (12) is zero. (This neglects homogeneous solutions, which correspond to Debye screening near the electrodes.) With the left-hand side of Eq. (12) set to zero, Eq. (12) leads to

$$E=\frac{e}{\sigma_H/D_H+\sigma_S/D_S}\left(\frac{j_H}{D_H}-\frac{j_S}{D_S}\right). \tag{13}$$

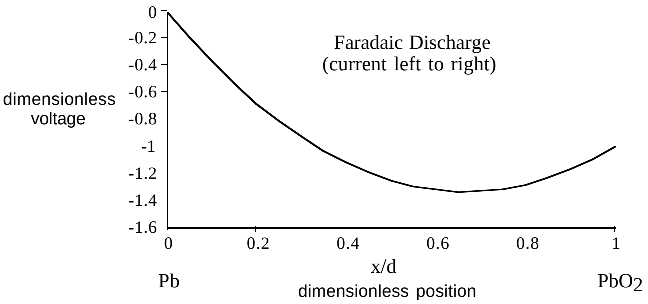

FIG. 1. Dimensionless voltage profile of Eq. (16) for faradaic discharge.

Using the specific j_H and j_S of Eq. (4), which carry current, the corresponding field E^I is found from Eq. (13) to be

$$E^I=\frac{ej_0}{\sigma_H/D_H+\sigma_S/D_S}\left[\left(\frac{1}{D_H}+\frac{1}{D_S}\right)+\left(\frac{1}{D_H}-\frac{1}{D_S}\right)\frac{2x}{d}\right]. \tag{14}$$

Equation (8) then yields the voltage profile $V^I(x)$ due to current I,

$$\begin{aligned}V^I(x)-V^I(0)&=-\int_0^x dxE^I(x)\\&=-\frac{ej_0/d}{(\sigma_S/D_S+\sigma_H/D_H)}\left[\left(\frac{1}{D_H}+\frac{1}{D_S}\right)xd\right.\\&\quad\left.+\left(\frac{1}{D_H}-\frac{1}{D_S}\right)x^2\right].\end{aligned} \tag{15}$$

Using $n_H=n_S=0.3\times10^{28}/\mathrm{m}^3$ (corresponding to a well-charged cell, 35% H_2SO_4 by weight) and Eq. (11), Eq. (15) yields $\sigma_H/D_H=\sigma_S/D_S=1.87\times10^{10}\ \mathrm{s}/\Omega\ \mathrm{m}^3$. Further, $D_S=1.3\times10^{-9}\ \mathrm{m}^2/\mathrm{s}$, $D_H=9.3\times10^{-9}\ \mathrm{m}^2/\mathrm{s}$, so $D_H\approx7D_S$. This leads to $\sigma_S=24.7(\Omega\ \mathrm{m})^{-1}$ and $\sigma_H=176.6(\Omega\ \mathrm{m})^{-1}$, values appropriate to dilute acid [10–12].

Since E varies linearly in space, it has a nonzero divergence, and therefore, by Gauss's Law, a nonzero charge density: local electroneutrality does not apply.

Note that, for the present sign conventions, during discharge I and j_0 go rightward, with $V^I(d)-V^I(0)<0$ and upward (positive) curvature; current and voltage difference both reverse during charge. Equation (15) yields $\Delta V=|V^I(d)-V^I(0)|=(2ej_0d/D_H)/(\sigma_S/D_S+\sigma_H/D_H)$. For $ej_0=10\ \mathrm{A/m}^2$ and $d=1$ mm, Eq. (15) yields $|V^I(d)-V^I(0)|=0.057$ mV. Figure 1 depicts a dimensionless form of the voltage profile of Eq. (15),

$$\tilde{V}^I(x)-\tilde{V}^I(0)=-\frac{1}{2}\left[\left(1+\frac{D_H}{D_S}\right)\left(\frac{x}{d}\right)+\left(1-\frac{D_H}{D_S}\right)\left(\frac{x}{d}\right)^2\right]. \tag{16}$$

This case corresponds to discharging, where the Pb electrode is on the left and the PbO_2 electrode is on the right.

Basically, $\Delta V=ej_0d/\sigma_H$, and since $\sigma_H\sim n_H$, for fixed d the quantity j_0/n_H determines ΔV. Also, the fractional change in n_H after time t is $\delta n_H/n_H=j_0t/n_Hd$

$=(j_0/n_H)(t/d)$. Hence, if we increase ΔV, then we increase $\delta n/n_H$ in proportion. Since the values $ej_0=10$ A/m^2 and $d=1$ mm give $\delta n_H/n_H \approx 0.4\times 10^{-4}$, we can either increase the current or decrease the concentration by a factor of 2000 and still have $\delta n_H/n_H=0.08$. This increases ΔV to 114 mV, a rather appreciable value.

At sufficiently low concentrations that the H_2SO_4 is doubly ionized, and hence the electrode reactions differ from those considered here, for slow steady surface reactions the above reasoning still applies, although the detailed field, voltage, and charge density differ [15].

III. NONFARADAIC REACTIONS

Reference [1] assumed that the only ionic currents at the electrodes are those associated with electric current flow (faradaic reactions). If only faradaic reactions occur, then the voltage profile across the cell should be uniform in the absence of current flow. In the present section we show that, for non-current-carrying (nonfaradaic) reactions, theory predicts a quadratic voltage profile even in the absence of current flow. Note that the nonfaradaic reactions satisfy $j_H=j_S$ [so that by Eq. (5) there is zero net electric current]. Faradaic discharge depends upon the pore size within the electrodes, and thus varies with the state of the battery. A well charged (poorly charged) battery is expected to have large (small) pores and a large (small) nonfaradaic reaction rate.

At the Pb plate we expect the nonfaradaic reaction [10,11]

$$\mathrm{Pb}+\mathrm{HSO_4}^{-}+\mathrm{H}^{+}\rightarrow \mathrm{PbSO_4}+\mathrm{H_2}. \tag{17}$$

Corresponding to this, in the slow, steady regime

$$j_S(x)=j_H(x)=j_H^{Pb}\left(1-\frac{x}{d}\right), \tag{18}$$

where the hydrogen flux $j_H^{Pb}<0$ at the Pb electrode because the H^+ ions flow leftward to react with the Pb electrode (cf. Fig. 1). For j_H and j_S in Eq. (18), which correspond to reactions only at the Pb plate, Eq. (13) yields a field

$$E^{Pb}=\frac{ej_H^{Pb}}{\sigma_H/D_H+\sigma_S/D_S}\left(\frac{1}{D_H}-\frac{1}{D_S}\right)\left(1-\frac{x}{d}\right). \tag{19}$$

This field leads to a voltage

$$V^{Pb}(x)-V^{Pb}(0)=-\frac{ej_H^{Pb}d}{\sigma_S/D_S+\sigma_H/D_H}\left(\frac{1}{D_H}-\frac{1}{D_S}\right)\times\left(\frac{x}{d}-\frac{x^2}{2d^2}\right). \tag{20}$$

With $j_H^{Pb}<0$, Eq. (20) leads to the dimensionless form $-2(x/d)+(x/d)^2$ given in Fig. 2. It corresponds to $V^{Pb}(d)>V^{Pb}(0)$ and upward (positive) curvature.

At the PbO_2 plate, we expect the nonfaradaic reaction [10,11]

$$\mathrm{PbO_2}+\mathrm{H}^{+}+\mathrm{HSO_4}^{-}\rightarrow \mathrm{H_2O}+\mathrm{PbSO_4}+\tfrac{1}{2}\mathrm{O_2}. \tag{21}$$

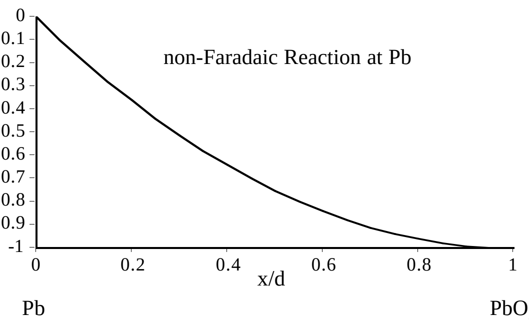

FIG. 2. Dimensionless voltage profile $-2(x/d)+(x/d)^2$ for nonfaradaic discharge associated with ion flow to the Pb electrode.

Correspondingly, in the slow, steady regime

$$j_S(x)=j_H(x)=j_H^{PbO_2}\left(\frac{x}{d}\right), \tag{22}$$

where the hydrogen flux $j_H^{PbO_2}>0$ at the PbO_2 electrode because the H^+ ions flow rightward to react with the PbO_2 electrode. For j_H and j_S in Eq. (21), which correspond to reactions only at the PbO_2 plate, Eq. (13) yields a field

$$E^{PbO_2}=\frac{ej_H^{PbO_2}}{\sigma_H/D_H+\sigma_S/D_S}\left(\frac{1}{D_H}-\frac{1}{D_S}\right)\frac{x}{d}. \tag{23}$$

This field leads to a voltage

$$V^{PbO_2}(x)-V^{PbO_2}(0)=-\frac{ej_H^{PbO_2}d}{\sigma_S/D_S+\sigma_H/D_H}\left(\frac{1}{D_H}-\frac{1}{D_S}\right)\times\left(\frac{x^2}{2d^2}\right). \tag{24}$$

With $j_H^{PbO_2}>0$, Eq. (24) leads to the dimensionless form $(x/d)^2$ given in Fig. 3. It corresponds to $V^{PbO_2}(d)>V^{PbO_2}(0)$ and upward (positive) curvature.

For both nonfaradaic reactions E varies linearly in space, so it has a nonzero divergence, and therefore, by Gauss's Law, a nonzero charge density; local electroneutrality is violated.

For all three of these reactions (one faradaic and two nonfaradaic), the quadratic component of the voltage is signifi-

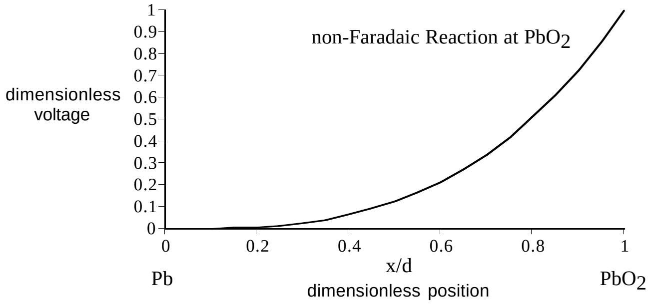

FIG. 3. Dimensionless voltage profile $(x/d)^2$ for nonfaradaic discharge associated with ion flow to the PbO_2 electrode.

cant because the diffusion coefficients D_H and D_S are rather different. If they were the same, there would be no quadratic term.

It is possible to estimate the nonfaradaic discharge rate from the rule of thumb that a lead-acid battery ''spontaneously'' discharges (due to these very reactions) at about 1% per day. Assuming a battery with a full charge of 60 A h at 12 V, a single 2 V cell contains eight subcells, each with full charge of 7.5 A h at 2 V. The nonfaradaic discharge rate $e(|j_H^{Pb}|+|j_H^{PbO_2}|)A$ is thus $0.01(7.5A\ \text{h})/24\text{h}=3.125\times10^{-3}$ A. Then $A=100\ \text{cm}^2$ gives $e(|j_H^{Pb}|+|j_H^{PbO_2}|)=0.3\ \text{A/m}^2$. This rate is small compared to characteristic faradaic discharge rates. An estimate of the total voltage drop across the sample, due to both nonfaradaic surface reactions, is $\Delta V^{NF}\approx[e(|j_H^{Pb}|+|j_H^{PbO_2}|)d][D_H/D_S-1]/4\sigma_H$, which yields $\Delta V^{NF}\approx13.6\ \mu$V. Although small, this voltage is nevertheless measurable. An electrode design having pores smaller by a factor of two but with the same macroscopic area would have about four times the effective area for reactions, and thus four times the reaction rate and hence $\Delta V^{NF}\approx55\ \mu$V.

IV. CONCLUSIONS

For a planar geometry we have shown how slow, steady ordinary (nonfaradaic, or noncurrent producing) surface reactions produce ionic fluxes that vary linearly in space. The linear spatial variation of the ionic fluxes then leads to an electric field and to ionic density gradients that also vary linearly in space. The linear spatial variation of the electric field then leads both to a quadratic voltage profile and to a uniform volume charge density; the latter implies that local electroneutrality does not hold. One consequence of this result is that properties of a battery can be studied by monitoring its voltage profile even when it is not charging or discharging. It is essential, however, that the ion diffusivities be different, as is the case for a slowly charging or discharging lead-acid cell.

Note that in an electrochemical cell most of the voltage drop occurs across the double-layer regions at each electrode-electrolyte interface. (Similarly, for a semiconductor-metal interface, most of the adjustment takes place within the lower conductivity material.) [16] Our present interest is in the much smaller voltage drop across the cell itself.

To our knowledge there have not yet been any experiments of this sort, wherein voltage profiles within the cell itself (rather than across the working electrodes). To ensure that the predicted quadratic dependence is observed, at least four equally spaced and nominally identical measuring electrodes (e.g., platinum or sulfated lead) should be placed within the electrolyte. Before any measurements are taken with the cell in place, the baseline relative voltages of the electrodes should be established (i.e., in distilled water or in sulfuric acid of nominally uniform concentration). In addition, when the measuring electrodes are in place, it must be established that their readings are indeed proportional to the actual local voltage within the electrolyte. This conclusion may require consideration of the double-layers at the measuring electrodes, and how they are affected by ion flow.

The prediction that slow, steady nonfaradaic reactions can lead to nontrivial voltage profiles has broad implications. Monitoring of batteries without electrical discharge has been mentioned, as has voltages induced in a sample by oxygen intake at surfaces. Moreover, biological growth sites attract chemicals. They thus serve as electrodes, with reactions that are either faradaic or nonfaradaic (or a linear combination of the two), according to whether or not the individual ionic currents produce a net electric current. Hence one can expect electric fields to be associated with biological growth, as indeed has been observed [17].

ACKNOWLEDGMENTS

I would like to thank Joe Ross, Allan Jacobson, and Joel Cohen for valuable conversations. This work was supported in part by the Department of Energy from DOE Grant No. DE-FG03-96ER45598.

---

[1] W.M. Saslow, Phys. Rev. Lett. **76**, 4849 (1996).
[2] W.M. Saslow, Phys. Rev. B **59**, 15 160 (1999).
[3] W.M. Saslow, Phys. Rev. E **59**, R1343 (1999).
[4] L.E. Kinzler, A.F. Frey, A.B. Coppens, and J.V. Sanders, *Fundamentals of Acoustics*, 3rd ed. (Wiley, New York, 1982), p. 225.
[5] W.M. Saslow, Phys. Rev. B **27**, 588 (1983).
[6] J. Newman, Trans. Faraday Soc. **61**, 2229 (1965); W.H. Smyrl and J. Newman, *ibid.* **63**, 207 (1967).
[7] J.-N. Chazalviel, Phys. Rev. A **42**, 7355 (1990).
[8] S.R. in't Hout, J. Appl. Phys. **79**, 8435 (1996).
[9] I. Lyubomirsky, V. Lyahovitskaya, and D. Cahen, Appl. Phys. Lett. **70**, 613 (1997).
[10] H. Bode, *Lead-Acid Batteries* (Wiley, New York, 1977).
[11] G.W. Vinal, *Storage Batteries*, 4th ed. (Wiley, New York, 1955).
[12] J. Newman, *Electrochemical Systems*, 2nd ed. (Prentice-Hall, Englewood Cliffs, NJ, 1991), Sec. 11.8. The author considers a one-one electrolyte, such as silver nitrate, with silver electrodes, so that the nitrate is not transported. For small currents, so that the transport equations can be linearized, exact solution yields that there is *no* deviation from local electroneutrality (i.e., deviations can occur only to second order in the current amplitude).
[13] Y. Yang and W.M. Saslow, J. Chem. Phys. **109**, 10331 (1998).
[14] I. Yokota, J. Appl. Phys. **16**, 2213 (1961).
[15] W.M. Saslow (unpublished).
[16] See *Comprehensive Treatise of Electochemistry*, edited by O'M. Bockris, B.E. Conway, and E. Yeager (Plenum, New York, 1980), Vol. 1.
[17] E.J. Lund, *Bioelectric Fields and Growth* (University of Texas Press, Austin, TX, 1947).