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Enhanced electrical current densities in electrochemical systems through the use of nanostructured electrodes

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A model is proposed regarding electrical current from an electrochemical device. The current density, J is explained through electric field induced ion drift in the electrolyte bulk. The resulting equation is largely consistent with, but not identical to, the conventional equation based on ion diffusion at the electrode surface. Experiments using nanostructured electrodes display larger J than conventionally thought possible, which can be explained through the drift-based equation. Our study points to the consequent utility of electrodes comprised closely spaced nanostructures.

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An important problem in modern day science and technology, related to energy capacity, concerns both increasing the amount of stored electrical charge as well as enhancing the rate at which the charge could be taken up or released. In this regard, fuel cells or batteries¹ has been acknowledged to be prototypes for high energy concomitant with low power capabilities, brought about by charge storage in the bulk and diffusion related limitations, respectively. Alternately, electrical capacitors have contrary attributes, i.e., through being recognized as low energy and high power devices, mediated through the charge being located at/close to the surface. It then seems to be clear that obtaining both high energy and power could be facilitated through electrochemical reactions that are not diffusion limited. As diffusion is essentially a bulk or volume based phenomena,² alternate mechanisms for charge storage mainly operate through increasing the effective surface area, e.g., through either enhancing the number of charge storage sites on the surface,³ or through using thin layer electrochemical models⁴ where all the charge is stored in the intervening electrolyte between closely spaced structures and diffusion is unnecessary for reactions on the surface.

It is then understood that the essential elements underlying charge storage and transfer involve the interaction of ions in the electrolyte with the electrode through either diffusion to the surface and subsequent electrochemical reaction or the latter alone (as in the thin layer case), under the influences of forces⁵ due to a concentration gradient or electric field, respectively. In this paper, we seek to re-examine the fundamentals of charge transfer in terms of electric field induced ion drift from the bulk of the electrolyte. We intend to show that such drift currents would dominate the diffusion currents in the bulk. The resulting new equation is consistent with the conventional equation derived from the completely different regime of diffusion current at the electrode surface. In comparison to experiment, we find that the drift-based equation can explain a broader spectrum of data.

We consider an electrode with a net charge density per unit volume Q_m in contact with an electrolyte of total charge density Q_{ion} ,⁶ as in Figure 1(a). While the formation of an electrical double layer⁴ on the surface of an electrode, due to charge compensation or screening from the electrolyte, is reasonably well understood, the spatial distribution of the ions may be complex. We examine a simplified version where the ions do not perfectly screen the electrode charge, i.e., $Q_{ion} < Q_m$, and a one-dimensional charge variation. We assign the spacing between the electrodes to be L , and that between the edges of the double layers to be L' , implying that the thickness of the double layer, t_{dl} on an electrode would be, on average, equal to $(L - L')/2$, where $2t_{dl} \ll L$.

The variation in electric field E in the device ($0 < x < L$) in both the double layer E_{dl} and the electrolyte E_{el} , as in Figure 1(b), can be obtained from $E = \int_0^x \frac{\rho}{\epsilon} dx$, with ρ as the respective charge density ($= Q_m$ or Q_{ion}) and ϵ being the equivalent and uniform dielectric permittivity.⁷ When Q_{ion} is only slightly smaller than Q_m , E_{dl} would be significantly larger than E_{el} . Further spatial integration leads to the potential profile $V(x) = -\int_L^x E dx$, with the potential of the counter electrode set to a reference value of zero as in Figure 1(c). Consistent with $E_{dl} > E_{el}$, the voltage across the double layer V_{dl} would be significantly larger than that across the electrolyte V_{el} . It is to be noted that the applied voltage across the electrodes/device is $V_{app} = 2V_{dl} + V_{el}$.

As the charge distribution in the double layer is related to the electrolyte ion radius and to thermal fluctuations, it occurs over spatial scales typically several orders of magnitude smaller than the device length, so there is no appreciable difference between representing the double layer to be of a finite width vs. that of a sharply peaked distribution for the purposes of partitioning V_{app} . Nonetheless, the shape of Q_{ion} in Figure 1(a) reflects the fixed electrical double layer closer to the electrode—reckoned with respect to the outer Helmholtz plane, and the adjacent diffuse double layer with an exponential decay in the ion concentration.⁴

We define γ as a measure of the screening strength⁸ of the electrode charge through

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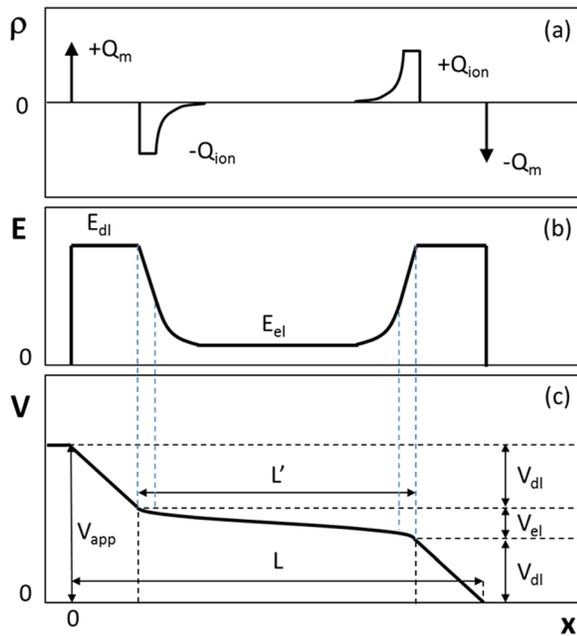


FIG. 1. (a) Schematic representation of the charge density ρ , with electrode charge Q_m and electrolyte ion Q_{ion} . L is the total device length. (b) The electric field E , with double-layer field E_{dl} and electrolyte field E_{el} . E is symmetric, and L' is the length excluding the double-layers. (c) The electric potential V , with double-layer potential $2V_{dl}$ and electrolyte potential V_{el} . The counter electrode is assigned a reference potential of zero.

$$\gamma = \frac{V_{el}}{V_{app}}. \quad (1)$$

Considering that $V_{app} \approx 2t_{dl}E_{dl} + L'E_{el}$, $V_{el} \approx L'E_{el}$, $E_{dl} = Q_m/\epsilon$, and $E_{el} = (Q_m - Q_{ion})/\epsilon$, we can also derive

$$\frac{Q_{ion}}{Q_m} = 1 - \frac{2t_{dl}}{L'} \frac{\gamma}{1 - \gamma}. \quad (2)$$

In this form, with $\gamma = 0$, $Q_{ion}/Q_m = 1$, meaning that the double layer holds exactly as much charge as the electrode and we have perfect screening; there would no driving force for an electrochemical redox (reduction-oxidation) reaction in this case. With $\gamma = L'/L$, $Q_{ion}/Q_m = 0$, meaning that there is no screening whatsoever of the electric field from the double-layer to the bulk electrolyte. Note that γ cannot be equal to 1 in this formulation.

We now study the behavior of ions in the electrolyte under the influence of E_{el} , which induces a drift velocity $\dot{x} = \mu E_{el}$, with μ being the ion mobility. Then, the electrical current density is $J = q(CN_A)\dot{x}$ with $q = ne$, where n is the charge per ion, e is the elementary electronic charge, C is the bulk electrolyte molar concentration, and N_A is the Avogadro number. We regard a typical experiment in electrochemistry, e.g., cyclic voltammetry (CV) which can determine the complete electrochemical behavior of a system⁴ and is often used to monitor the nature and reversibility of the cathodic and anodic reactions in an electrolyte.^{9,10} CV involves a linear sweep of V_{app} , recording the net electrical current through the electrodes. The rate of change of the voltage, i.e., the scan rate $\nu = dV_{app}/dt$, can be related to E_{el} using Eq. (1) by

$$E_{el} = \frac{dV_{el}}{dx} = \frac{d(\gamma V_{app})}{dx} = \gamma \frac{dV_{app}/dt}{dx/dt} = \frac{\gamma \nu}{\dot{x}}. \quad (3)$$

It is assumed that γ is spatially independent, since neither V_{el} nor V_{dl} are spatially dependent. Then, $\dot{x} = \mu E_{el} = \mu \frac{2\nu}{\dot{x}}$ so that $\dot{x} = \sqrt{\gamma \mu \nu}$. This new \dot{x} is converted into J through $J = q(CN_A)\dot{x}$. Further, through the Einstein relation $\mu = \frac{qD}{k_B T}$ and the equality $\frac{F}{RT} = \frac{e}{k_B T} = \frac{q/n}{k_B T}$, where D is the diffusion coefficient, k_B is the Boltzmann constant, T is the temperature, F is the Faraday constant, and R is the gas constant, yields

$$J = \sqrt{\gamma} \cdot C \sqrt{F^3 \frac{D\nu}{RT}} n^{\frac{3}{2}}. \quad (4)$$

Such a form for the current density has been previously established through invoking elaborate semi-infinite diffusion based techniques and cited in literature^{4,11,12} as the Randles-Sevcik (R-S) equation $J = a \cdot C \sqrt{F^3 \frac{D\nu}{RT}} n^{\frac{3}{2}}$, with a being a numerical constant. This equation is defined by mapping the redox reaction current to a diffusion current anchored to the electrode surface. The device operates in a closed circuit, so the currents thus defined at one surface are related to the currents at the opposing surface. It is possible to find an analytical integral equation for device current as a function of time $i(t)$, after which the normalized current may be numerically plotted as a function of t . The normalized peak current⁴ involves an $a = 0.4463$; the corresponding peak current density is hereby defined as J_{peak} . Therefore, there is no empirical parameter involved in a .

We have now shown that electric field induced drift in the bulk electrolyte could yield a similar form for J , reinforcing the deep connection between drift and diffusion. Assuming an equivalence of our derived relation Eq. (4) with the R-S equation, we can now assign a physical significance for the constant a

$$\sqrt{\gamma} \text{ (proposed drift model)} = a \text{ (R - S equation)}. \quad (5)$$

For example, a match of the R-S equation's a coefficient in J_{peak} of 0.4463 with $\sqrt{\gamma}$ leads to $\gamma \sim 0.2$. In general, a larger value of γ corresponds to a larger value of V_{el} , though it is limited by V_{app} as in Figure 2. Equivalently, J increases if

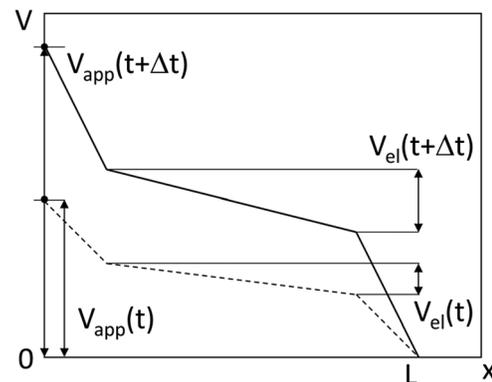


FIG. 2. Comparing voltage profiles at times t and $t + \Delta t$, the increase in V_{app} is always greater than that for V_{el} . In general, a faster scan rate ν allows for a larger value of γ and thus V_{el} due to weaker screening.

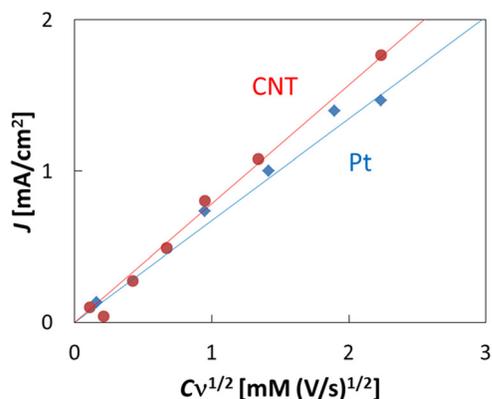


FIG. 3. Current density J as a function of the product of the $\text{K}_3\text{Fe}(\text{CN})_6$ molar concentration C and the square root of scan rate $\sqrt{\nu}$. Data from Ref. 8 by Hoefler and Bandaru. Flat Pt and nanostructured CNT electrode data are compared to the drift model in Eq. (4).

screening can be weakened without affecting the other factors in Eq. (4).

The imperfect screening of Q_m by Q_{ion} causes V_{el} to be a fraction of V_{app} . At larger ν , the screening is further weakened since the ions cannot respond to the quicker change in V_{app} , resulting in a larger value of E_{el} and a larger ionic current density. Generally, the electric field induced drift current density J_{drift} may be assumed to be dominant over the diffusion current density J_{diff} from the bulk electrolyte, i.e., outside the double layer. This can be understood by taking the ratio of $J_{drift} = q(CN_A)\mu \frac{dV_{el}}{dx} \approx q(CN_A)\mu \frac{\gamma V_{app}}{L}$ to $J_{diff} = qD \frac{d(CN_A)}{dx} \approx q \frac{k_B T}{q} \mu \frac{CN_A}{L}$, which is equal to $\gamma \frac{V_{app}}{k_B T/q}$. At $T = 300$ K, by assuming a typical experimental input of $V_{app} = 1$ V, $k_B T/q \sim 26/n$ mV, so we have $J_{drift}/J_{diff} \sim 40\gamma/n$. For such electrolytes as $\text{K}_3\text{Fe}(\text{CN})_6$, $n = 1$ for the positive ions and 3 for the negative ions. If $\gamma \sim 0.25$, as indicated and also justified later in the paper, then $J_{drift}/J_{diff} = 10/n \gg 1$. As a result, for the assumed bias conditions, basing the total current on drift current would be appropriate. The above formulations and conclusions apply to both positive and negative ions, albeit with different μ and n .

Comparison of our drift model to experimental current densities was used for additional insight into the nature and variation of γ . J vs. $C\sqrt{\nu}$ is plotted from experimental data for both flat Pt electrodes and for nanostructured carbon nanotube (CNT) electrodes in Figure 3. Empirically, $J = 0.674 C\sqrt{\nu}$ for Pt and $J = 0.786 C\sqrt{\nu}$ for CNT. Assuming the same diffusion coefficient $D = 6.8 \times 10^{-6}$ cm^2/s for both positive and negative ions⁴ and using $F = 96487$ C/mol, $R = 8.31$ J/mol K, and $T = 300$ K, from Eq. (4) we have $\sqrt{F^3 \frac{D}{RT}} = 1.56 \left[\frac{\text{mA}/\text{cm}^2}{\text{mM}\sqrt{\text{V}/\text{s}}} \right]$. Therefore, $J = \sqrt{\gamma} 1.56 C\sqrt{\nu}$ for both Pt and CNT. For Pt, $\sqrt{\gamma} \sim 0.4327$, ($\gamma \sim 0.2$), in close accord to the theoretical R-S value of $a = 0.4463$ as in Eq. (5). However, for CNT, $\sqrt{\gamma} \sim 0.5045$ and thus $\gamma \sim 0.25$. The experimental procedures as well as the relevant parameters and data for the fitting were taken from papers by Hoefler and Bandaru.^{3,13} The precision to four significant figures is in keeping with the coefficient of

the R-S equation. The CNT electrode consists of CNTs with average length, diameter, and separation³ of 25 ± 4 μm , 20 ± 5 nm, and 150 ± 50 nm.

A greater value of $\gamma \sim 0.25$ for CNT compared $\gamma \sim 0.2$ for Pt indicates that the screening of the electrode has been weakened, allowing a larger electric field in the electrolyte. The consequent larger magnitude of E_{el} and J_{drift} could account for the larger current densities of Figure 3 for the nanostructured electrodes. It is to be noted that the figure suggests that the slopes of $J(C\sqrt{\nu})$ plots may be different for the two experiments, i.e., for Pt electrodes computed using the traditional methodology and for CNT electrodes analyzed through the newer formulation. The close spacing of the CNTs could result in a relative starvation of the screening ions from the electrolyte yielding a greater value of γ and suggests design methodologies to further increase electrical current densities.

In summary, we have indicated the principles through which the net current density of electrochemical devices can be analyzed by ionic drift current from the bulk electrolyte. A metric γ , related to the ratio of the potential drop in the electrolyte to that of the applied voltage, has been introduced through which the current density increase, in terms of $\sqrt{\gamma}$, may be parameterized. A preliminary comparison between flat electrodes and nanostructured electrodes seems to indicate larger current densities for the latter, which can be explained more readily through $\sqrt{\gamma}$. However, reduced electric field screening is fundamental to the improved electrical current densities. Further optimization of the nanostructured electrode based electrochemical devices considering such principles and based on the fact that the theoretical upper limit for $\sqrt{\gamma}$ approaches unity, would be worthy of continued study.

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