Chemical Physics Letters 695 (2018) 24–27

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Electron tunneling in nanoscale electrodes for battery applications

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ARTICLE INFO

Article history:
Received 16 December 2017
In final form 25 January 2018
Available online 31 January 2018

ABSTRACT

It is shown that the electrical current that may be obtained from a nanoscale electrochemical system is sensitive to the dimensionality of the electrode and the density of states (DOS). Considering the DOS of lower dimensional systems, such as two-dimensional graphene, one-dimensional nanotubes, or zero-dimensional quantum dots, yields a distinct variation of the current-voltage characteristics. Such aspects go beyond conventional Arrhenius theory based kinetics which are often used in experimental interpretation. The obtained insights may be adapted to other devices, such as solid-state batteries. It is also indicated that electron transport in such devices may be considered through electron tunneling.

1. Introduction

The use of nanostructured materials as electrodes in energy storage devices [1], such as batteries and electrochemical capacitors [2], is typically based on considerations related to a large ratio of the surface area to the volume. An optimal packing of the nanostructures, spanning scales and dimensionality, is necessary to ensure both a large mass-based as well as volume-based energy density, as well as the seamless passage of a large magnitude of concomitant electrical current. Considering the relevance of multi-dimensional current passage, careful attention needs to be paid to the relevant mode of charge transfer both within the electrode, as well as from the electrode to an electrolyte. Generally, electron/carrier transfer occurs when filled states on one side and empty states on the other are aligned [3]. Such an alignment is shifted by an applied voltage difference, *i.e.*, the overpotential, between the electrode and electrolyte. The relationship is reversible, and may be observed experimentally through techniques such as chronoamperometry [4–6]. While a theory of electron transfer has been posited based on perturbation theory [7], such formulations typically consider a constant density of states [8] (DOS) in the electrode and a continuum of energy states in the electrolyte [3]. However, in nanostructures, the DOS is highly variable, *e.g.*, as related to the quantum capacitance C_Q [9] in single-layer graphene [10], and non-smooth variations/oscillations of the electrochemical rate constant were predicted in one-dimensional carbon nanotubes, due to chirality dependent DOS [8]. It is the aim of this paper to clarify such foundational aspects, probe alternate viewpoints, and interpret experimental results.

Conventional models, *e.g.* Butler-Volmer (BV) [4], Marcus-Hush (MH) [11–13], or Marcus-Hush-Chidsey (MHC) [5,14] kinetics, express traditional electrode battery operation through chemical reaction dynamics, which is chiefly considered through the reaction rate constant k (1/s). These models employ phenomenological constants to relate to the underlying electrochemical processes. This approach is well suited for traditional electrode materials but may not be appropriate for nanomaterials. For instance, in the BV model, α and β are electron transfer coefficients for the chemical reaction (backward and forward, respectively), where $I = I_0\,(e^{-\alpha\eta} + e^{\beta\eta})$ and $\alpha + \beta = 1$, where η is the overpotential. They represent the ease of reducing the potential barrier for the backward and forward chemical reaction, respectively. In the MH/MHC models, the reorganization energy λ (eV) is taken as a measure of the configurational change related to the species undergoing the redox (*ox*idation or *red*uction) reaction. The Chidsey formalism [5] considers electron occupancy by invoking the Fermi-Dirac distribution, *i.e.*, with $f(E) = 1/(\exp[(E - E_F)/k_BT] + 1)$, with electron energy E, Fermi energy E_F, and thermal energy k_BT. For metallic electrodes, implicitly assuming constant DOS ρ (1/eV) is reasonable. Under this assumption, k saturates when $|\eta| > \lambda/e$, where e is the elementary charge.

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https://doi.org/10.1016/j.cplett.2018.01.054
0009-2614/

2. Analytical representation of current

However, such an assumption may be unsuitable for nanostructured electrodes. Recent experimental $k-\eta$ characteristics for single-layer graphene (SLG) electrodes [6,14] do not saturate, and instead monotonically increase with η. A better understanding of such aspects is achieved below by introducing an energy-dependent DOS. The details of this new theory will be presented elsewhere [15].

We first consider the relation between the k and an observed electrical current I (A) to reconcile the experimental data with the energy-dependent DOS theory. k is the net chemical reaction rate for a redox reaction involving oxidized O and reduced R ion species as in $O + e^- \rightleftharpoons R$, and is often experimentally determined [4–6] as a time decay constant. For such a reaction,

$$I = FA[k_f C_O - k_b C_R], \tag{1a}$$

where C_O and C_R (mol/m^2) are the molar concentrations of the O and R species, respectively, and k_f and k_b (1/s) are the forward and backward reaction rate constants, respectively. F (C/mol) is the Faraday constant, and A (m^2) is the electrode-electrolyte contact surface area. For the determination of k_f or k_b alone, large negative or positive η is used, whereby Eq. (1a) reduces to

$$I = en_{2D}Ak, \tag{1b}$$

where n_{2D} (1/m^2) is the area density of the relevant ion species and $k = k_f$ or k_b. The nanostructured experimental data may thus be written equivalently in terms of k or I.

When considering charge transfer through electron transport, I is defined as

$$I = eAnv, \tag{2a}$$

where n (1/m^3) is the electron carrier density and v (m/s) is the electron velocity. The shift from k to v allows us to discuss spatial coordinates. However, such a specific form is relevant for current flow through a homogeneous material. I from the electrode to the electrolyte (or vice versa) may be broadly described through an equation of the form

$$I = eAnv\Theta, \tag{2b}$$

with Θ as the tunneling probability of the electrons participating in the redox reaction [16,17].

Considering Eq. (2b) in more depth, it is necessary to use both $f(E)$ and the DOS for both the electrode and the electrolyte to determine A, n, and v, as well as the coefficient from Fermi's Golden Rule to determine v and Θ [18–21]. Consequently,

$$I_{lt} = e\int [f_{eld} \times A\ell D_{3D}] \frac{2\pi}{\hbar} M^2 [(1-f_{rdx}) \times \rho] dE, \tag{3a}$$

$$I_{rt} = e\int [(1-f_{eld}) \times A\ell D_{3D}] \frac{2\pi}{\hbar} M^2 [f_{rdx} \times \rho] dE. \tag{3b}$$

Here, I_{lt} represents left-going current (right-going electrons) and I_{rt} represents right-going current (left-going electrons). The equation explicitly considers the electrode DOS $D(E)$ (1/(eV m^3)) and occupancy probability f_{eld} (E) with Fermi energy E_F, and the electrolyte DOS (integrated over volume) $\rho(E)$ (1/eV) and occupancy probability $f_{rdx}(E)$ with redox energy E_{rdx}. Depending on the dimensionality of D, a spatial normalization representing the active electrode region is multiplied, *e.g.* a volume $A\ell$ (3D), an area A (2D), a length ℓ (1D), or nothing (0D), such that the normalization times D has units of 1/eV. $\hbar$ (eV s) is the Planck constant, and the matrix element of interaction M (eV) couples the electrode and electrolyte energy levels, smaller in magnitude compared to the level broadening, and hence considered to be relatively energy independent [22]. The electrolyte properties and matrix element together represent the Fermi's Golden Rule, which describes electron transfer rate. Moreover, for the occupancy probability distribution, the Fermi-Dirac distribution was considered over the Boltzmann distribution for both electrode and electrolyte to represent the occupancy of the states, and implicitly considers electron – electrolyte interactions.

Typically, ρ may be considered through a Gaussian: $\rho(\Delta E) = \rho_0 \exp[-(\Delta E)^2/(4\lambda k_B T)]$. The ΔE is related to the deviation of a redox species electron energy from the most probable energy, corresponding to say, that for reduction (*red*) or oxidation (*ox*), *i.e.*, $\Delta E = \Delta E_{red}$ (= $E_{red} - E^o_{red}$) or $\Delta E = \Delta E_{ox}$ (= $E_{ox} - E^o_{ox}$). The electrolyte DOS is represented through two peaks for the *red* and *ox* levels, which may be correlated to electron affinity and ionization energy, with a range of energies and corresponding states. Moreover, the possibility of a solid electrolyte may be easily understood through considering the ρ of a solid as well as replacing E_{rdx} with another

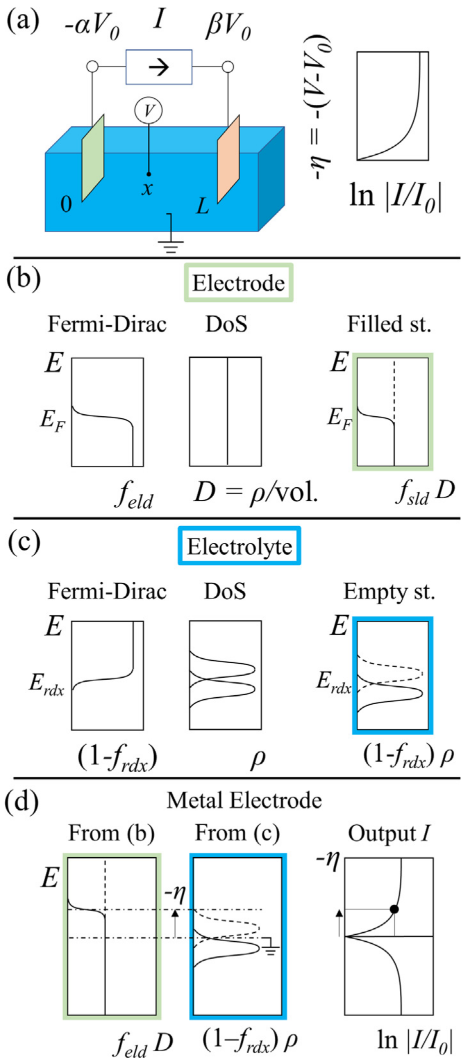

Fig. 1. (a) The consideration of electrode dimensionality of nanoscale electrodes, together with electrode-electrolyte interactions in a typical electrochemical system (*e.g.*, a battery or capacitor), yields novel electrokinetics. α and β are electron transfer coefficients for the voltage, most often used in the Butler-Volmer model; $\alpha + \beta = 1$. The consequent electrical current I with respect to an overpotential η (with the standard redox potential as a reference) and normalized to I_o, the current at η = 0, is due to the mutual overlap of the carrier density from the electrode with the electrolyte. (b) The product (*right*) of the electrode Fermi-Dirac function $f_{eld}(E)$ (*left*) and DOS $D(E)$ (*middle*). D can be converted to units of eV^{-1} by multiplying electrode volume for a 3D material. (c) The product (*right*) of the reverse of the electrolyte Fermi-Dirac function $1 - f_{rdx}(E)$ (*left*) and DOS $\rho(E)$ (*middle*). (d) ln $|I/I_o|$, represented by the convolution (*right*) of f_{eld} D (*left*) and $(1 - f_{rdx})$ ρ (*middle*).