Journal of Electroanalytical Chemistry 799 (2017) 333–348

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Exact identities between values of the tunnel current in the redox-mediated tunneling contacts and the positions of the extrema of the tunnel current/overvoltage characteristics

Igor G. Medvedev

The A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences, Leninsky prospect 31, 119071 Moscow, Russia

ARTICLE INFO

Keywords:
Redox-mediated tunneling contacts
Tunneling current
Reorganization energy
Exact identities
Tunnel current/overvoltage characteristics
The points of extrema

ABSTRACT

Two exact identities for the tunnel current through a redox-mediated tunneling contact are obtained. These identities are valid for arbitrary temperatures, electrodes, strengths of the redox group-electrodes coupling, interaction of the valence electrons with the phonon modes and values of the Coulomb repulsion U between electrons at the valence level. They permit to obtain the expression which relates the positions of different maxima (minima) of a given tunnel current/overvoltage characteristic in the case of the symmetric tunneling contact defined below or relates the positions of maxima (minima) of two tunnel current/overvoltage characteristics where one of them corresponds to the transposed parameters describing two working electrodes and their coupling to the redox group. For the symmetric tunneling contacts and under the other general conditions we also obtain the expression for the position of one of the extremal points of the tunnel current/overvoltage characteristic. It is shown that this point is the point of the maximum in the case of the redox-mediated tunneling contacts considered at room temperature within the spin-less model or the model with $U = 0$. The tunnel current/overvoltage characteristics are calculated both for the fully diabatic and fully adiabatic limits and it is shown that the positions of the points of the maxima (minima) are indeed given by the derived expressions.

1. Introduction

The study of the redox-mediated tunneling contacts based on the single molecule and pioneered by Tao [1] is very important due to their potential use as the elements of the new molecular electronics [2–8]. It is connected both with the possibility of the independent variations of the two potential drops (the bias voltage between the electrodes as the source-drain voltage and the electrode potential of one of the electrodes relative to the third electrode as the gate voltage) and the possibility of the operation in the condensed matter environment at room temperature (in situ systems). Therefore, a large number of works were devoted to the experimental and theoretical study of the tunnel current/overvoltage and the current/bias voltage characteristics (see, e.g., the articles [4–16] and references therein as well as the recent papers [17–20]) for in situ tunneling contacts. In particular, the use of the electrochemical gating permits to reveal such properties as rectification and amplification of the tunnel current so that, as was first noted in Refs. [21–23], the redox-mediated tunneling contacts can be considered as the molecular transistors.

The characteristic feature distinguishing in situ systems from the vacuum tunneling contacts is the strong interaction of the tunneling electron with the fluctuation of the polarization of the condensed matter environment. It is just this interaction which permits the transitions of the redox group (RG) from the oxidized state to the reduced one. Therefore, the first theoretical study of the electron tunneling through a one-level RG [24] was based on the picture of the sequential electron tunneling consisting in the intermediate electron localization at the RG after thermal fluctuations and subsequent full relaxation of the vibrational subsystem corresponding to the fluctuations of the polarization of the condensed matter environment. This picture describes the fully diabatic electron transitions (ETs) (the limit of the weak interaction of the RG with the working electrodes when the RG valence level moves very fast across the energy window) and was further elaborated in Refs. [25–27,9,11,13,16,28]. In particular, the classical rate equation method was used in [26] for the derivation of the expression for the tunnel current for the spin-less model and the study of the current/bias voltage and current/overvoltage relations. This study was generalized in Ref. [9] where the effect of the Debye screening of the electrode potential in the tunneling gap was taken into account within the linear approximation. Effect of the Coulomb repulsion between two electrons located at the valence orbital of the RG, effect of the asymmetry of the coupling of the RG with the working electrodes and the

E-mail address: theor@elchem.ac.ru.

http://dx.doi.org/10.1016/j.jelechem.2017.06.025
Received 18 November 2016; Received in revised form 13 June 2017; Accepted 16 June 2017
Available online 17 June 2017
1572-6657/

band structure effect on the tunnel current was studied in Refs. [11,13,15–16,28]. The classical rate equation method used in this works is formulated in terms of the rate constants of the non-adiabatic electron transfer at each working electrode and is valid only in the fully diabatic limit [29] (see also a more detailed discussion in [16]).

However, the classical rate equation method with the use of the rate constants of the adiabatic electron transfer was also adopted for the fully adiabatic ETs (the limit of the strong interaction of the RG with the working electrodes) in the large number of works (see, e.g., Refs. [26,21]). This approximation being very clear and physically transparent is not formally correct for the fully adiabatic ETs although it involves a number of new concepts including the description of the mechanism of the tunneling of a "boost" of electrons. On the other hand, in this case the electron jumps between the electrodes are much faster than the shift of the valence level due to the electron-phonon interaction so that the electrons "see" the almost fixed valence level of the RG in this case. Therefore, the resonant tunneling model is a more appropriate here. Its variant which uses the average only over the density of the oxidized states of the RG was considered in [30]. However, as was argued in [26,21], the account of both valence states is necessary. Later the tunnel current in the strong coupling limit was calculated based on the simulations of the stochastic motion of the classical phonon subsystem [31]. A more natural way of the calculation of the tunnel current for the fully adiabatic limit was suggested in Ref. [32] where the total steady state current was obtained using the thermal averaging of the partial tunnel current calculated at a given set of the phonon coordinates over the Boltzmann distribution of the phonon coordinates described by the exact adiabatic free energy surface (AFES) which determines the phonon motion. The dependence of the tunnel current on the bias voltage, overvoltage, the width of the valence level of the RG, the reorganization energy was studied and discussed for arbitrary values of the parameters and arbitrary particular cases [32–34].

The explicit expressions for the tunnel current obtained both for the fully diabatic [9,11,16,28] and fully adiabatic [32–34] ETs show a number of the exact identities which connect the tunnel current values corresponding to different choice of the parameters describing the tunnel contact. These identities were first presented in [11,32] for the classical phonon modes and the fully diabatic and fully adiabatic ETs, respectively. They were generalized in [16] to the case of the asymmetric tunneling contacts with the asymmetric coupling of the RG to the electrodes. The first goal of the present paper is the proof of these exact identities for arbitrary temperatures, arbitrary values of the energy U of the Coulomb repulsion between the electrons having different spin projections and located at the valence orbital of the RG, arbitrary phonon modes and the arbitrary types of the ETs (including the intermediate case between the fully diabatic and the fully adiabatic ETs and taking into account the possibility of the asymmetric coupling of the RG to the electrodes) at the working electrodes having arbitrary band structure. These identities are proved below within the Anderson-Holstein model [35–36] which, in particular, implies the local linear screening of the RG charge by the harmonic oscillators describing the fluctuations of polarization of the condensed matter environment without the account of the effect of the inharmonicity.

The proved identities are important in themselves. However, they permit us to obtain the expression which relates the positions of different maxima (minima) of a given tunnel current/overvoltage characteristic in the case of the symmetric tunneling contact (the case of the symmetric coupling of the RG to the electrodes whose bands can be obtained from each other using a mirror transformation with respect to their centers) or relates the positions of maxima (minima) of two tunnel current/overvoltage characteristics where one of them corresponds to the transformed parameters describing two working electrodes and their coupling to the RG. As one of the consequences of this relation, we also obtain the expression for one of the points of extrema η_{extr} of the tunnel current/overvoltage characteristic which is valid for arbitrary conditions mentioned above but for the symmetric tunneling contact. The derivation of these expressions is the second goal of the present paper. In the experimental investigation of Tao [1] it was first shown that the maximum of the tunnel current/overvoltage dependence η_{max} is close to the equilibrium potential of the redox group (i.e., $\eta_{max} \approx 0$). This result was confirmed by the theoretical study of the relationship between the tunnel current and overvoltage performed in Ref. [26] for the fully adiabatic limit of the spin-less model within the classical rate equation method. The dependence of the η_{max} on the bias voltage V was also found out:

$$\eta_{max} = (0.5 - \gamma)V/\xi. \tag{1}$$

Here the parameters ξ and γ describe the fraction which the overvoltage and the bias voltage contribute to the shift of the valence level of the RG due to the interaction of the RG with the electrostatic potential existing in the tunnel gap and the overvoltage η is determined as the "cathodic" overvoltage $\eta = \varphi_L{}^0 - \varphi_L$ where $\varphi_L{}^0$ and φ^L are the "equilibrium" potential of the left electrode and its potential, respectively. Later the same result for η_{max} was reproduced in Ref. [32] for the case of the fully adiabatic limit within a more consistent approach and in Ref. [9] for the case of the fully diabatic ETs in the limit of the large reorganization energy E_r of the classical phonon modes of the solvent.

The result presented by Eq. (1) has been supported by a number of experimental studies. Not only the maximum itself has been observed but the dependence of the position of the maximum on the bias voltage has also been investigated (see, e.g., Refs. [37–39,18]). However, in such experiments it is unknown what a regime of the electron transfer is at play. Indeed, it may be the fully diabatic, the fully adiabatic or the intermediate one. We show that, at room temperature, Eq. (1) takes place within the spin-less model for arbitrary regimes of the ETs but for the symmetric tunneling contacts. As the illustration of this result we calculate the tunnel current/overvoltage characteristics in the wide-band approximation for the spin-less model for both the fully diabatic and the fully adiabatic ETs and demonstrate that Eq. (1) is valid for arbitrary strengths of the electron-phonon coupling. Similar calculations are performed for the case when $U = 0$ which is the simplest example of the account of the electron spin projections. We also present the results of calculations of the tunnel current/overvoltage characteristics for the asymmetric tunneling contacts and show that the relations between the positions of the points of maxima (or minima) as well as the relation between the corresponding values of the tunnel current are fulfilled.

The paper is organized as follows. In Section 2 we describe the model and present the identities for the tunnel current which are proved in Appendices A and B. In Section 2 we also derive the expressions for the points of the extrema of the tunnel current/overvoltage dependence. In Section 3 we verify the obtained expressions for the case of the spin-less model within the fully diabatic and fully adiabatic limits of the ETs. In Section 4 we perform the analogous checking both for the case of non-zero U in the fully diabatic limit and for the case when $U = 0$. The concluding remarks are presented in Section 5.

2. The model and the identities for the tunnel current

We consider the case when the single-electron energy level spacing in the RG is sufficiently large so that only one spin-degenerate valence level of the RG is taken into account. The system is described by a well-known Anderson-Holstein Hamiltonian [35–36]:

$$H = \sum_{p,\sigma,\alpha} \varepsilon_{p\alpha} c^+_{p\sigma\alpha} c_{p\sigma\alpha} + \sum_{\sigma} \left[\varepsilon_b(q_k) n_\sigma + \frac{1}{2} U n_\sigma n_{-\sigma} \right] + \sum_{p,\sigma,\alpha} (V_{p\alpha} c^+_\sigma c_{p\sigma\alpha} + V^*_{p\alpha} c^+_{p\sigma\alpha} c_\sigma) + \frac{1}{2} \sum_k \hbar\omega_k (p_k^2 + q_k^2) \tag{2}$$

where $\varepsilon_{p\alpha}$ are the electronic energies of quasi-particle states $|p\alpha>$ of