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Determination of density of electronic states using the potential dependence of electron density measured at nonzero temperatures

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A method of calculation of one-particle density of states has been developed and tested. Using this method a density of states can be calculated from a potential dependence of electron density measured at nonzero temperature. The method can be applied to a system with an externally controlled chemical potential such a as porous electrode penetrated with an electrolyte.

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In many important materials such as conducting polymers,[1,2] quantum dot assemblers,[3] and porous semiconductors,[4] the one-particle density of states (DOS) plays a key role for the description of electrical, photovoltaic, and thermodynamic properties and determines the operation of the devices. One of the methods for determination of the DOS is based on the measurement of a variation of a density of electrons (holes) caused by a variation of Fermi energy (ε_F).[5] This method has been applied in many works for investigation of the DOS in conducting polymers,[6] quantum dots,[7] and porous semiconductors.[5,8–10] Another method extracts the DOS from the potential dependence of the current tunneling from a metal electrode into an investigating material through a thin barrier.[11] Finally, in both methods one measures the dependence of the amount of carries (amount of available states) on Fermi energy (applied potential). Taking a derivative of this dependence one gets a value usually considered to be equal to the density of states. However, the latter is, in general, valid only at zero temperature ($T=0$), when a distribution function $f((\varepsilon-\varepsilon_F)/kT)$ is steplike. At finite temperature the distribution function is smeared in an energy range of width about kT (k denotes the Bolzmann constant). For example, in Fig. 1(c) a result of such a differentiation denoted as g_0 is shown for a density of states consisting of two Gaussian peaks [Fig. 1(a)]. At finite kT, g_0 looks quite different from the DOS, although kT is clearly less than the distance between peaks. Thus, the temperature broadening of the distribution function can lead to a significant error in the determination of the DOS.

In this paper we describe a method to extract the one-particle density of states, which utilizes experimentally measured quantities and accounts for nonzero temperature. The method should be especially useful in systems where measurements cannot be performed at low temperatures, for example, in porous electrodes penetrated with electrolytes. As an example, the experimental results of the measured electron density in nanostructured $\mathrm{TiO_2}$ as a function of the potential will be analyzed and discussed.

In what follows we will, for concreteness, describe the determination of the DOS from the dependence of electron density (n) on the applied potential (U) measured in a porous electrode penetrated with an electrolyte or other conducting medium so that electrical field is screened and $U=-\varepsilon_F/e$ (e denotes the elementary charge). However, the proposed approach can be also applied to the tunneling experiments. At finite temperature the electron density depends on the applied potential, DOS $g(\varepsilon)$, temperature, and distribution function $f((\varepsilon+eU)/kT)$:

$$n(U)=\int_{-\infty}^{\infty} g(\varepsilon) f\left(\frac{\varepsilon+eU}{kT}\right) d\varepsilon = kT\int_{-\infty}^{\infty} g(kTx-eU) f(x)dx, \tag{1}$$

where ε is the energy, which is taken equal to zero at the bottom of conduction band and decreases downwards in the band gap. An essential assumption is that the energy of a state does not depend on chemical potential, i.e., we neglect many-particle effects. The latter allows changing a variable in the integral.

Expression (1) is an integral equation with respect to density of states. At sufficiently low temperatures its solution can be obtained in a form of series of powers of T. Taking a derivative of Eq. (1) versus U one gets

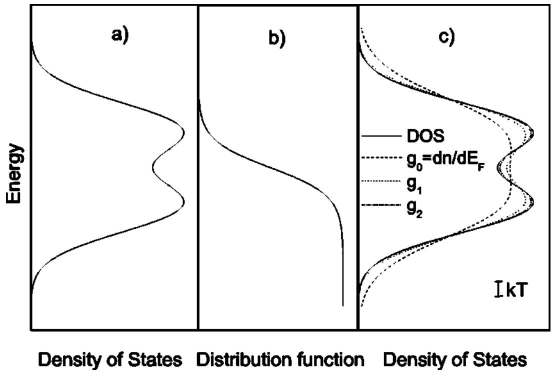

FIG. 1. (a) Simulated DOS. (b) Fermi-Dirac distribution function at finite T. (c) Simulated DOS and its approximations determined from a dependence of number of occupied states on Fermi energy: $g_0=dn/d\varepsilon_F$; g_1 and g_2—described in the text.

TABLE I. Comparison of approximate and exact densities of states at energy −0.25 eV.

Temperature (eV)	g_0 (10^{19} cm^{-3}/eV)	g_1 (10^{19} cm^{-3}/eV)	g_2 (10^{19} cm^{-3}/eV)	g_3 (10^{19} cm^{-3}/eV)	Exact DOS (10^{19} cm^{-3}/eV)
0.1	0.136	0.126	0.090	0.075	0.082
0.08	0.134	0.107	0.080	0.078	0.082
0.06	0.1243	0.0895	0.0793	0.0817	0.0821
0.04	0.1052	0.0820	0.0817	0.0821	0.0821
0.02	0.087740	0.081751	0.082085	0.082085	0.082085

$$\frac{dn}{dU} = -ekT\int_{-\infty}^{\infty}\frac{dg}{d\varepsilon}f(x)dx = e\int_{-\infty}^{\infty}g(kTx-eU)\frac{df}{dx}dx, \qquad (2)$$

where partial integration was used for transformation of the expression (2) and we take into account that $f(\infty)=0$, $g(-\infty)=0$, $f(-\infty)=1$.

Since the temperature is suggested to be low, one can expand the integral in expression (2) in a Taylor series with respect to kT:

$$\int_{-\infty}^{\infty}g(kTx-eU)\frac{df}{dx}dx$$
$$= \int_{-\infty}^{\infty}g(-eU)\frac{df}{dx}dx + \sum_{l=1}^{\infty}(kT)^l\frac{1}{l!}\frac{d^l}{d(kT)^l}$$
$$\times\left(\int_{-\infty}^{\infty}g(kTx-eU)\frac{df}{dx}dx\right)\Bigg|_{kT=0}. \qquad (3)$$

Introducing a derivative into each term of expression (3), one gets

$$\frac{dn}{dU} = -e\left(g(-eU) + \sum_{l=1}^{\infty}a_l\ \frac{d^{2l}g}{d\varepsilon^{2l}}\Bigg|_{\varepsilon=-eU}(kT)^{2l}\right), \qquad (4)$$

where

$$a_l = -\frac{1}{(2l)!}\int_{-\infty}^{\infty}x^{2l}\frac{df}{dx}dx. \qquad (5)$$

The solution of Eq. (4) has to be found as an expansion in the Taylor series of kT. This can be done by the method of series iterations. As a zero-order approximation one has the result usually applied in which the density of states is given by the chemical capacitance[5,8–10]

$$g_0(-eU) = -\frac{1}{e}\frac{dn}{dU}. \qquad (6)$$

Then substituting $g_0(-eU)$ into Eq. (4), the first order approximation $g_1(-eU)$ can be found from the equation

$$\frac{dn}{dU} = -e\left(g_1(-eU) + a_1(kT)^2\ \frac{d^2g_0}{d\varepsilon^2}\Bigg|_{\varepsilon=-eU}\right). \qquad (7)$$

This gives

$$g_1(-eU) = -\frac{1}{e}\left[\frac{dn}{dU} - a_1\left(\frac{kT}{e}\right)^2\frac{d^3n}{dU^3}\right]. \qquad (8)$$

This procedure can be continued and the solution has a form

$$g(-eU) = -\frac{1}{e}\left[\frac{dn}{dU} + \sum_{l=1}^{\infty}b_l\frac{d^{2l+1}n}{dU^{2l+1}}\left(\frac{kT}{e}\right)^{2l}\right]. \qquad (9)$$

Some coefficients b_l are listed below. The numbers are calculated for usual Fermi-Dirac distribution function $f(x)=1/[\exp(x)+1]$:

$$b_1 = -a_1 = -1.644\,493\,4,$$

$$b_2 = -(a_2 - a_1{}^2) = 0.811\,742\,4,$$

$$b_3 = -(a_3 - 2a_1a_2 + a_1{}^3) = -0.190\,751\,8,$$

$$b_4 = -(a_4 - 2a_1a_3 - a_2{}^2 + 3a_1{}^2a_2 - a_1{}^4) = 0.026\,147\,85,$$

Expression (9) is valid at least at temperatures less than $\Delta\varepsilon/k$, where $\Delta\varepsilon$ is a characteristic width of the change of the DOS. Although validity of Eq. (9) is questionable at higher temperatures, it is obvious that differentiation of $n(U)$ will make features of the density of states hidden at finite temperature more visible.

To examine the accuracy of expression (9) a potential dependence of electron density was calculated for an exponential distribution of states:

$$g(\varepsilon) = \frac{N_t}{\varepsilon_0}\exp\left(\frac{\varepsilon}{\varepsilon_0}\right) \qquad (10)$$

and the Fermi-Dirac distribution function using expression (1). Derivatives d^pn/dU^p have been calculated by numerical integration. Then density of states has been calculated using expression (9) with a different number of terms. The result has been compared with an exact DOS given by expression (10). The results are listed in Table I. The width of the distribution ε_0 was taken equal to 0.1 eV, and $N_t=10^{19}$ cm^{-3}. Zero energy corresponds to the bottom of conduction band. It is seen that the accuracy of the approximation for the DOS increases quite fast with an increase of number of terms in series (9). Further, even at $kT=\varepsilon_0$ 10% accuracy is reached with four terms.

We have also tested the proposed method for a density of states consisting of two Gaussian peaks [Fig. 1(a)]. For a smeared distribution function [Fig. 1(b)] we calculated first-

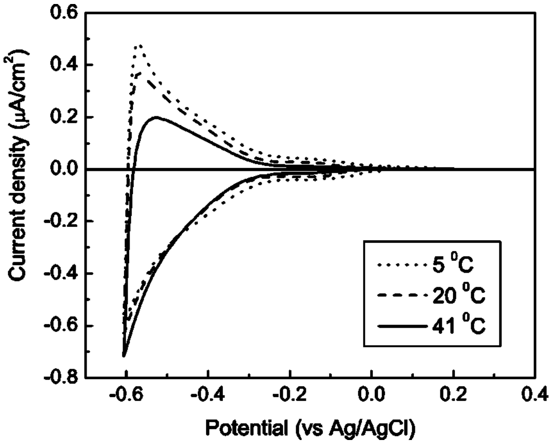

FIG. 2. Experimental cyclic voltamograms recorded in nanoporous $\mathrm{TiO_2}$ at 5, 20, and 41 °C. Scan rate 0.1 mV/s.

and second-order approximations g_1 and g_2, which are shown in Fig. 1(c) together with $g_0 = dn/d\varepsilon_F$ and the exact DOS. One can see that already g_2 almost coincides with the exact DOS.

The derivation of the density of states from experimental data requires knowledge of high-order derivatives of function $n(U)$. Since experimental data contain noise, a certain smoothing is required to perform digital differentiation of higher orders. A promising alternative approach would be direct measurement of derivatives by analyzing the higher harmonics of ac current.

To illustrate the procedure described above we apply it to analyze cyclic voltamograms (CV) recorded on nanoporous $\mathrm{TiO_2}$ permeated with inert pH 2 $\mathrm{HClO_4}$ aqueous solution containing $0.2M$ $\mathrm{LiClO_4}$. The nanoporous $\mathrm{TiO_2}$ consisted of a film with sintered 20-nm-diam anatase crystals, prepared as reported previously[12] on a conducting substrate. Experimental curves are presented in Fig. 2. The film potential is measured with respect to a Ag/AgCl reference electrode. Temperature variation was less than 0.1 °C. The position of the $\mathrm{TiO_2}$ conduction band bottom at this pH is −0.51 V, as determined by spectroelectrochemical measurements.[8,13] The first derivative dn/dU has been calculated from the charging part of CV using the following expression:

$$\frac{dn}{dU} = \frac{I}{eLS}\left(\frac{dU}{dt}\right)^{-1}, \tag{11}$$

where I is current, $L = 1.56\ \mu\mathrm{m}$ is the thickness of porous $\mathrm{TiO_2}$ layer, $S = 0.969\ \mathrm{cm}^2$ is the area of porous $\mathrm{TiO_2}$, and $dU/dt = 0.1$ mV/s is the scan rate. Higher-order derivatives have been calculated using the five point averaging procedure. Figure 3 shows the first three approximations g_0, g_1, and g_2 for the DOS calculated using expression (9) with coefficients b_l calculated for the Fermi-Dirac distribution function. It is seen that features of the DOS become much more pronounced with an increasing number of terms in the series. Further, a conclusion can be drawn that the DOS of porous $\mathrm{TiO_2}$ is quite different from exponential distribution. Note that the difference between g_1, and g_2 is much less than the difference between g_0 and g_1, which is evidence of the convergence of the series (9).

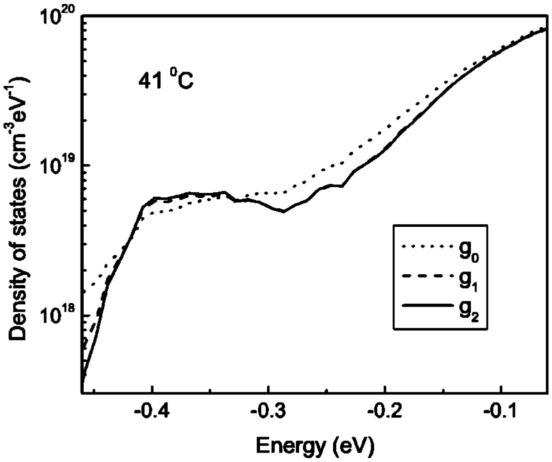

FIG. 3. DOS calculated for nanoporous $\mathrm{TiO_2}$ at 41 °C from the cyclic voltamogram using series (9) with different numbers of term (1, g_0; 2, g_1; and 3, g_2). The energy origin is the lower edge of the conduction band.

If the distribution function is chosen correctly, expression (9) should give the same results for different temperatures. Figure 4 presents g_2, an approximation for the DOS calculated using $n(U)$ curves measured at 5, 20, and 40 °C. Coefficients b_l calculated for the Fermi-Dirac distribution have been used. One can see that the g_2 approximation for the DOS is indeed temperature dependent. The temperature dependence of g_2 persists also for the distribution function $f(x) = 1/\left[\frac{1}{2}\exp(x) + 1\right]$, which is valid for doubly degenerate and once occupied states. The following reasons can explain the temperature dependence of g_2: (1) The distribution function for some states in the band gap is different from a simple Fermi-Dirac function due to degeneracy (for example, the degeneracy is more than 2). (2) The one-particle density of states is really temperature dependent (for example, due to Coulomb interaction between electrons in $\mathrm{TiO_2}$ and ions in electrolyte).

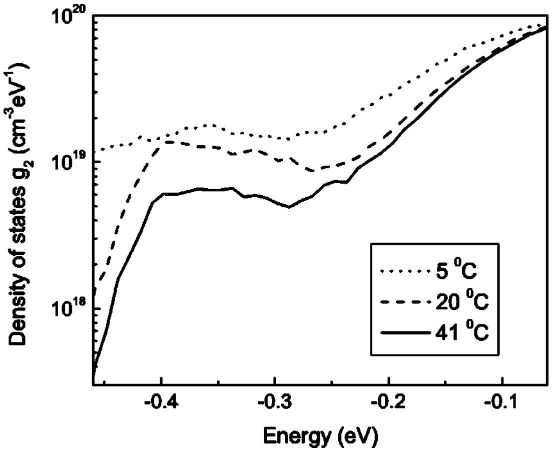

FIG. 4. DOS g_2 calculated from the cyclic voltamogram recorded on nanoporous $\mathrm{TiO_2}$ electrodes using the first three terms of series (9). The energy origin is the lower edge of the conduction band.

From our determination of the DOS in nanoporous TiO_2 (anatase) shown in Fig. 4, we obtain at 41 °C a distribution decreasing faster than exponential below the edge of the conduction band, and then displaying a maximum at 350 meV below the conduction band edge. This last feature is related to the uncoordinated Ti^{4+}, which forms a nearly monoenergetic surface state.[10,14–16]

In conclusion a method of determination of the one-particle density of states using derivatives of $n(U)$ curves measured in heterogeneous systems at finite temperature has been presented. The method can be applied to the heterogeneous systems with a strong screening of the electrical field such as porous electrodes penetrated with electrolytes or any other system where the chemical potential can be controlled by an external electrical potential.

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[1] H. C. F. Martens, I. N. Hulea, I. Romijn, H. B. Brom, W. F. Pasveer, and M. A. J. Michels, Phys. Rev. B **67**, 121203 (2003).

[2] R. Menon, A. J. Heeger, K. H. Kim, Y. H. Kim, A. Schwartz, M. Dressel, and G. Grüner, Phys. Rev. B **61**, 1635 (2000).

[3] P. Guyot-Sionnest, M. Shim, C. Matranga, and M. Hines, Phys. Rev. B **60**, R2181 (1999).

[4] J. Nelson, Phys. Rev. B **59**, 15 374 (1999).

[5] J. Bisquert, Phys. Chem. Chem. Phys. **5**, 5360 (2003).

[6] J. Bisquert, G. Garcia-Belmonte, and Jorge Garcia-Canjadas, J. Chem. Phys. **120**, 6726 (2004).

[7] A. L. Roest, J. J. Kelly, D. Vanmaekelbergh, and E. A. Meulenkamp, Phys. Rev. Lett. **89**, 036801 (2002).

[8] F. Fabregat-Santiago, *et al.*, J. Phys. Chem. B **107**, 758 (2003).

[9] L. M. Peter *et al.*, J. Electroanal. Chem. **524–525**, 127 (2002).

[10] H. Wang *et al.*, J. Phys. Chem. B **105**, 2529 (2001).

[11] J. Mitra, A. K. Raychaudchuri, Ya. M. Mukovskii, and D. Shulyatev, Phys. Rev. B **68**, 134428 (2003).

[12] I. Abayev *et al.*, Phys. Status Solidi A **196**, R4 (2003).

[13] G. Rothenberger, D. Fitzmaurice, and M. Grätzel, J. Phys. Chem. **96**, 5983 (1992).

[14] G. Redmond, D. Fitzmaurice, and M. Grätzel, J. Phys. Chem. **97**, 6951 (1993).

[15] G. K. Boschloo and A. Goossens, J. Phys. Chem. **100**, 19489 (1996).

[16] G. Boschloo and D. Fitzmaurice, J. Phys. Chem. B **103**, 2228 (1999).