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Effect of Particle Size on Electrode Potential and Thermodynamics of Nanoparticles Electrode in Theory and Experiment

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ABSTRACT

The particle size of electrode materials has a significant influence on the standard electrode potential and the thermodynamic properties of electrode reactions. In this paper, the size-dependent electrochemical thermodynamics has been theoretically investigated and successfully deduced electrochemical thermodynamics equations for nanoparticles electrode. At the same time, the electrode potential and thermodynamical properties of Ag_2O/Ag nanoparticles electrode constructed by the solid and spherical Ag_2O nanoparticles with different sizes further testified that the particle size of nanoparticles has a significant effect on electrochemical thermodynamics. The results show that the electrode potential depends on that of the smallest nanoparticle in a nanoparticles electrode which consisted of different particle sizes of nano-Ag_2O. When the size of Ag_2O nanoparticles reduces, the standard electrode potentials and the equilibrium constants of the corresponding electrode reactions increase, and the temperature coefficient, the mole Gibbs energy change, the mole enthalpy change and the mole entropy change decrease. Moreover, these physical quantities are all linearly related with the reciprocal of average particle size ($r > 10$ nm). The experimental regularities coincide with the theoretical equations.

1. Introduction

In the traditional theory of electrochemical thermodynamics, it has been widely recognized that a standard electrode potential (E^o) is a constant, such as $E^o_{Ag_2O/Ag}$ is 0.342 V [1].

But in recent years, the reported results have showed that the standard electrode potential can be changed when the particle size of electrode reaches to nanometer scale for its strong surface effect. Henglein [2–5] made numerous researches on the electrochemical properties of metal particles; shifts in the redox potential were identified successfully to offer an explanation during his working on the unusual catalytic performances of small particles. Plieth [6,7] studied the electrode potential of metal nanoparticles, associating the variations in electrode potential with those in surface area, finally found the relationship between shifts in electrode potential and particle radius based on the connection between electrode potential and change of Gibbs energy. Peter et al. [8] studied the electrochemical natures of Ag colloidal particles in a conductive medium experimentally. He discovered a negative shift in the electrode potential of Ag particles, in addition, small metal nanoparticles are more likely to be oxided than the bulk metal. Chaki et al. [9] also believed that there are some differences of the electrochemical performances between metal nanoparticles and corresponding bulk metal, and discussed the shifts in standard electrode potential for Ag particles with diameter less than 10 nm qualitatively. Rafael et al. [10] testified that Au particles with diameter less than 4 nm had an oxidation potential of 850 mV, demonstrating large negative shift. Sun et al. [11] formed a single gold nanoparticle, and electrochemical study revealed that the small Au particle has extraordinary stability compared with that of a bulk Au phase. It has been found also in our previous study that the size of particles which composed an electrode has a certain effect on electrode potential and electrochemical properties, and some thermodynamic relations were derived, the order of magnitude of influence of particle size on the electrode potential was estimated [12–14].

However, theoretical studies about the thermodynamics of nanoparticles electrode has not been yet perfect, especially, the influence of the particle size of nanoparticles electrode on electrochemical thermodynamics has not been investigated systematically and experimentally.

In this paper, theoretically, the relation between particle size and electrochemical thermodynamics, such as E^o, electrode

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reaction equilibrium constant (K^o), corresponding temperature coefficient ($\left(\partial E/\partial T\right)_p$), mole Gibbs energy change ($\Delta_r G_m$), mole entropy change ($\Delta_r S_m$) and mole enthalpy change ($\Delta_r H_m$), is investigated and the electrochemical thermodynamics equations is deduced. At the same time, the electrode potential and thermodynamical properties of Ag_2O nanoparticles electrode constructed by Ag_2O nanoparticles with different particle sizes are investigated and compared with the theoretical relations.

2. Thermodynamical Analysis

2.1. Gibbs free energy of nanosystems

For a nanosystem consisting of N components and M kinds of dispersed phase, the total Gibbs energy can be described as [12],

$$G = G(T, p, n_B, A_k), \quad B = 1, 2, \cdots, N; \quad k = 1, 2, \cdots, M, \tag{1}$$

where, T is temperature, p is pressure, n_B is quantity of substance B, and A_k is the interfacial area of dispersed phase k. When the state changes, the change in G is given as,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n_B A_k} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n_B,A_k} dp + \sum_B \left(\frac{\partial G}{\partial n_B}\right)_{T,P,A_k,n_i \neq n_B} dn_B + \sum_k \left(\frac{\partial G}{\partial n_k}\right)_{T,P,n_B,A_j \neq A_k} dA_k i = 1, 2, \ldots, N; j = 1, 2, \ldots, M, \tag{2}$$

According to the classical chemical thermodynamics, the above expression can be rewritten as,

$$dG = -SdT + Vdp + \sum \mu_B^b dn_B + \sum \sigma_k dA_k, \tag{3}$$

where, μ_B^b and σ_k are the chemical potential of component B in block state (Without considering the surface effect) and the surface tension of dispersed phase k which is the specific surface Gibbs energy, respectively. For an electrochemical reaction, $dn_B = \nu_B d\xi$. If the electrochemical reaction is at constant temperature and pressure, the above expression can be simplified as,

$$dG = \sum \nu_B \mu_B^b d\xi + \sum \sigma_k dA_k, \tag{4}$$

where, ν_B denotes the stoichiometric number for substance B and ξ is the extent of reaction.

If dispersed phase k consists of a homogeneous pure substance B, the interfacial areas (A_k) of Eq. (4) can be considered as A_B, and the corresponding σ_k is σ_B. So Eq. (4) can be rewritten as follow:

$$dG = \sum \nu_B \mu_B^b d\xi + \sum \sigma_B dA_B. \tag{5}$$

Eq. (5) is divided by $d\xi$,

$$\Delta_r G_m = \sum_B \nu_B \mu_B^b + \sum_B \sigma_B \left(\frac{\partial A_B}{\partial \xi}\right)_{T,P} = \Delta_r G_m^b + \Delta_r G_m^s, \tag{6}$$

where, $\Delta_r G_m$ is total molar Gibbs energy change in an electrode reaction, $\Delta_r G_m^b$ the molar bulk Gibbs energy change and $\Delta_r G_m^s$ the molar surface Gibbs energy change.

If the dispersed phases are solid and spherical nanoparticles, then,

$$\left(\frac{\partial A_B}{\partial \xi}\right)_{T,P} = \frac{2\nu_B M_B}{\rho_B r_B}, \tag{7}$$

where, r_B, M_B, ρ_B are the particle radius, the molar mass and the mass density of dispersed phase B in an electrode. So,

$$\Delta_r G_m = \Delta_r G_m^b + \sum_B \frac{2\nu_B \sigma_B M_B}{\rho_B r_B}. \tag{8}$$

According to Eq. (8), when a dispersed phase is reactant, $\nu_B < 0$, the Gibbs energy change decreases with decreasing the particle size; otherwise, if the dispersed phase is product, the Gibbs energy change increases with decreasing the particle size.

2.2. Electrode potential of nanoparticles electrode

In the conditions of constant pressure and temperature, when an electrode reaction occurs reversibly, the change in Gibbs energy is equal to the reversible electric work, as follows,

$$\Delta_r G_m = -zEF, \tag{9}$$

where, z is charge transfer number, E is the electrode potential which nanoparticles take part in a electrode reaction, and F is the Faraday constant. According to Eq. (8), the electrode potential of a nanoparticles electrode can be expressed as,

$$E = E^b - \frac{1}{zF} \sum_B \frac{2\nu_B \sigma_B M_B}{\rho_B r_B}, \tag{10}$$

where, E^b is the electrode potential of ordinary electrode. According to the Nernst equation,

$$E = E^o - \frac{RT}{zF} \ln \prod a_B^{\nu_B} \tag{11}$$

$$E^b = E^{bo} - \frac{RT}{zF} \ln \prod a_B^{\nu_B}, \tag{12}$$

So, the standard electrode potential of the nanoparticles electrode can be expressed as,

$$E^o = E^{bo} - \frac{1}{zF} \sum \frac{2\nu_B \sigma_B M_B}{\rho_B r_B}. \tag{13}$$

In the condition of constant pressure and temperature, standard electrode potential of ordinary electrode is constant value, but standard electrode potential of nanoparticles electrode is related to particle sizes. If a dispersed phase in nanoparticles electrode is reactant, $\nu_B < 0$, the smaller the particle size is, the larger the standard electrode potential and the electrode potential are. On the contrary, the dispersed phase is product, the smaller particle size is, the smaller the standard electrode potential and the electrode potential are, too.

There is only one dispersed phase in the electrode reaction, Eq.13 can be simplified as

$$E^o = E^{bo} - \frac{2\nu_B \sigma_B M_B}{zF \rho_B r_B}. \tag{14}$$

We know that the σ_B is related to r_B, but when the particle size of dispersed phase is bigger($r > 10$ nm), the effect is very small, and the σ_B can be regarded as a constant approximately [15,16]. Then it can be seen from Eq. (14) that there is a linear relation between the standard electrode potential and the reciprocal of radius of nanoparticles.