

Thermodynamics in porous electrodes for one- and two-component electrolytes

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Thermodynamics of porous electrodes is different from that of planar electrodes. The main purpose of this study is to elucidate how porosity affects the thermodynamics in electrodes especially when the size of the pore is comparable to the size of the electrolyte ions. We consider only the cases where the electrical energy is stored in the form of electrical double layers (EDLs) and no Faradaic processes occur.

The effect of porosity on thermodynamics has been extensively studied for adsorption of gas molecules in porous materials. Thermodynamics of gas molecules in a porous material is different from that in the bulk because of the finite size effect and varying dimensionality, and the surface forces that are introduced by the porous media¹. For example, the pressure at which the gas shows capillary condensation varies depending on the pore size of the adsorbent. It is because of this fact that the surface area and the pore size distribution of porous materials can be estimated by gas adsorption methods.

The key thermodynamic fields for gas adsorption are temperature and chemical potential of the gas molecules as the exchange of energy between the porous material and the outside is expressed as

$$dE = TdS + \mu dN, \quad (1)$$

where E denotes energy of the porous material including the gas molecules inside it, T the temperature, S the entropy, μ the chemical potential of the gas molecules, and N the number of the gas molecules in the pore. When it turns to porous electrodes, an additional thermodynamic field, voltage, is added to this equation as

$$dE = TdS + \mu dN + \Phi dq, \quad (2)$$

where Φ denotes the voltage and q the charge induced on the surface of the porous electrode. Thus, the thermodynamics of porous electrodes can be discussed in a parallel fashion to that of adsorption of gas molecules in porous material by adding the extra term related to the charge induction.

It is rather recently that the thermodynamics of porous electrodes has been drawing particular attention. For many years, thermodynamic properties for unit surface area of the porous electrode have usually been considered independent of the porous structure. In fact, when the pore size is much larger than the thickness of the electrical double layers, this assumption is valid because the electrical field on the surface of the electrode does not propagate through the electrical double layers. In this case, the thermodynamics of porous electrode does not depend on the pore size. However, it has been experimentally shown that the thermodynamics of porous electrodes indeed depends on the pore size when the pore size is comparable to the size of the electrolyte ions². A number of experimental and theoretical works have been performed for studying this problem since then.

In order to study the mechanism of the pore size dependence of the thermodynamics in porous electrodes, we have developed a Monte Carlo simulation method in the constant-voltage grand-canonical ensemble by extending the method for studying adsorption in porous materials, using the parallel forms of equations 1 and 2 above. Using the method, we have qualitatively reproduced the pore size dependence of the thermodynamics that have

been found experimentally and have discussed the mechanism of that behavior³. We have also discussed the phase behaviors in porous electrodes⁴.

In this work, those studies were further extended to two component electrolytes and the characteristic features of multi-component electrolytes are discussed in comparison with those of one component electrolytes. The governing equation of the thermodynamics of a two-component system can be written as

$$dE = TdS + \mu_1 dN_1 + \mu_2 dN_2 + \Phi dq, \quad (3)$$

where the subscripts denote the two components. We found some thermodynamic behaviors that are similar to those of one component electrolytes such as the pore size dependence of the capacitance. Moreover, we also found other behaviors that are specific to multi-component systems. For example, it was found that the ratio of the content of the two components forming the electrical double layers changes as a function of thermodynamic parameters such as voltage. Those findings are discussed in relation to practical problems such as development of electrochemical capacitors or ion-selective adsorbents.

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