FEATURE ARTICLE

Scientific hints of developing supercapacitors

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Abstract
Since the research direction of supercapacitors (SC) has been deviated from the principle of causing capacitance, the revisit may be a future task in exploiting electric power storage. SC have been developed by applying ionic properties in order to enhance heterogeneity of ionic distributions. However, SC belong to double-layer capacitances (DLC), which are caused by orientation of solvent dipoles without any direct relation to ionic properties. DLC are always complicated with ion-independent characteristics such as frequency dispersion, voltage dependence, and participation in redox reactions, whereas these complications have not yet been considered in development of SC. Especially, pseudo capacitances should be examined through isolating the contribution of DLC from the redox properties.

Introduction

Future tasks are generally directed either to development of materials which have been exploited in other fields or to challenge along social requirements. If a present task is at a deadlock or runs short of scientific backgrounds, it should be regarded as a future task by incorporating basic concepts. SC belong to this category, in that they have been thought to be caused by heterogeneity of ionic distributions. Since they are based on DLC in principle, they should obey DLC, reflecting electric properties and thermodynamically averaged properties of solvents. Some complicated features of DLC should be also included in SC.

A critical task is a search for the contribution of Faradaic reactions to DLC, which is known as pseudo capacitances [1]. It is important to examine the dependence of DLC on Faradaic reaction, which has been classically regarded as independent. However, a question should be cast not only to the relation between the two but also to conditions of enhancement of pseudo capacitances from the thermodynamic viewpoints.

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Participation in ionic distribution

An electrochemical monograph describes SC as a member of DLC of which charge is stored by heterogeneous distribution of ions, discriminated from conventional capacitors composed of dielectrics. However, meticulously experimental results in the nineteenth century concluded that DLC electrochemically observed come from the inner layer rather than a diffuse layer with ionic distribution [2]. The former structure is still unknown in detail, whereas the latter can be estimated from Gouy-Chapman's theory. As a result, a source of DLC should be still ambiguous. There may be some technical reasons for paying attention to a contribution of ions. Enhancement of performance of SC needs to increase not only conductance of solution but also the affinity between carbon powder electrodes and solution. Consequently, utilized conditions of salts become inevitably targets of research, so that they may seem to control the performance, leading to apparent significance of ionic distribution.

The ambiguous attribution to the ionic distribution may be partially caused by a loss of well-defined experimental data for DLC, which depend not only on researchers but also techniques. The poor reproducibility lies in ambiguous seal of an electrode with insulators in order to expose a known area of the active electrode surface, as Grahame pointed out [3]. The seal is often so incomplete that solution permeates through a crevice between the electrode and the insulator to increase floating capacitance. Insertion of an electrode wire in solution avoids the poor reproducibility to demonstrate the effect of solvents on DLC [4, 5].

Frequency dispersion

DLC at a Pt wire electrode in KCl solution by current(I)-controlled charge and discharge show voltage(V)-time(t) curves composed of triangular waves, which can be predicted from the definition of the capacitance, $q (= It) = CV$ for a charge q. Then V should be proportional to t or C should be invariant to t. However, the triangular forms have $d^2V/dt^2 < 0$ for $I > 0$ or C increases with t. These variations can be found even for commercially available SC, but are hardly found for ceramic capacitors [6]. The time-dependence or frequency dispersion is explained in terms of the constant phase element [7]. It has been derived from the definition of the time-dependence of C for the applied ac-voltage, $V = V_0e^{\omega t}$, as $I = d(CV/dt) = V(i\omega C + dC/dt)$ [8]. Replacing t by $t' = 1/\omega$, we have $I/V = i\omega C - \omega^2 dC/d\omega$. Since the admittance is a simple sum of the imaginary part $i\omega C$ and the real one $\omega^2 dC/d\omega$, the equivalent circuit should be a parallel combination of the capacitive admittance of $i\omega C$ and the resistive one of $\omega^{-2}(dC/d\omega)^{-1}$. The resistance is observed as if it might occur in the double-layer thickness, but it is an apparent quantity resulting from the frequency dispersion. The experimental Nyquist plot shows a line, being a constant value of the slope, $1/\lambda$. Then the slope can be expressed by $\omega C/[-\omega^2 dC/d\omega] = 1/\lambda$. A solution of this differential equation yields $C = C_{1Hz}f^{-\lambda}$ [9]. This is the expression for the frequency dispersion, as shown in Fig. 1. The resistive component is necessarily involved in the ac-impedance data so far as a DLC is measured with time-variation of voltages. When the frequency is replaced by the time, the DLC is expressed by $C = C_{1s}t^{\lambda}$, where C_{1s} is the capacitance at $t = 1$ s. Thus, capacitance values obtained by constant currents always increase with the time, as have been measured in conventional charge-discharge curves of SC. The time-dependence should be examined in a future task because it is related with a leakage of SC through the double-layer resistance.
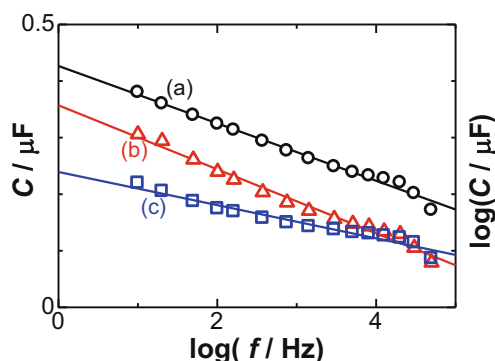

Fig. 1. Plots of log C for solvents of (a) DMSO, (b) propylene carbonate, and (c) dichloromethane including 0.1 mol dm^{-3} tetrahexylammonium perchlorate against log (f)

Variables of determining DLC

Possible parameters varying DLC are dc-potential, ac-voltages, ionic concentrations, ionic species, materials of electrodes, and kinds of solvents. It is Gouy-Chapman's theory that predicts U-shaped capacitance vs. dc-potential curves. Our experimental results, however, showed almost independent of dc-potentials [4, 5]. The variations with concentrations of salts exhibited independence of dc-voltage for concentrations more than 0.1 mM [10]. This observation implies that electrochemically observed DLC should not be controlled with Poisson-Boltzmann distributions of ions but should be determined by orientation of solvent dipoles. DLC at Pt, carbons, and transparent electrodes did not vary with kinds of halogen ions. Non-specific adsorption of F$^-$ may be valid only at mercury electrodes. Variations with dc-potentials have sometimes been observed at electrodes sealed with insulator, because of crevice between the electrode and the insulator.

Variation with ac-voltage should be distinguished from that with dc-potential, in that the former is used for determination of DLC at small ac-voltage, whereas the latter represents a total amount of oriented dipoles with the electric field. Dependence on dc-potential is revealed in charge-discharge curves by constant current control [6], and hence, it may be a significant variable for SC. Since the electric energy is given by $\int CV\,dV$, dependence on dc-potential should be discussed in the future for development of DLC.

The participation in orientation of solvent dipoles implies that DLC may depend on kinds of solvents. The examination of the dependence on 13 kinds of solvents showed that properties of solvents such as dielectric constants, viscosity, boiling temperatures, molar volume, or dipole moments had no simple relation with the DLC values [5]. A capacitance at the Helmholtz model, expressed by $C = \varepsilon/d$ (d: the thickness the inner layer), may indicate that d should correspond to the molecular length oriented in the direction of the electric field rather than thermodynamic variables. The usage of such values of d calculated from molecular models has provided the proportionality of C with $1/d$, as shown in Fig. 2 [5]. The smaller value of d enhances values of SC. However, this application is difficult because of unknown amounts of oriented dipoles.

Reason for frequency dispersion

Dipoles oriented by the electric field are not arranged regularly on an electrode; for example, a forward-oriented dipole makes the neighboring dipoles oriented in the reverse direction because of solvent-solvent interaction. Since the energy of field-orientation is smaller than the thermal energy (RT for the gas constant R) as well as solvent-solvent interactions and the hydrogen bonding energy, only a few fraction of dipoles are oriented by the electric field. Therefore, it is difficult to
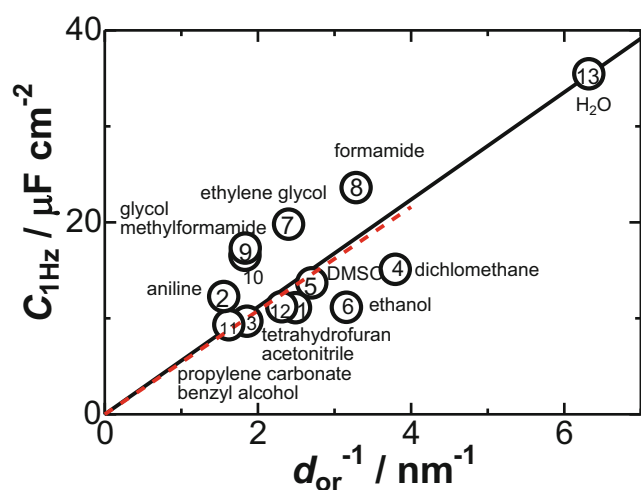
Fig. 2 Variations of C_{1Hz} with the inverse of the molecular length oriented in the field direction of 13 solvents

Fig. 3. Decrease in capacitance values caused by the redox reaction with the concentration of Fc-derivative, and the model of variations

control the arrangement of dipoles so densely that capacitive values become tremendously large.

The fluctuation by the other energies is a source of the frequency dispersion. Since a direction of a dipole is determined as a result of taking locally minimum energy through a huge number of molecular collisions, it takes a macroscopic time to reach the minimum. Therefore, DLC values continue to increase up to even second-order, leading to the term t^λ. This is a reason for why the time scale is much longer than nanosecond of the dipole inversion.

This concept can be realized through the semi-thermodynamic expression for the term t^λ [11]. The free-energy of the orientation of n dipoles is composed of the orientation enthalpy, nu_0, and the entropy of selecting n from the available N dipoles, i.e., $G_n = nu_0 - k_B T \ln(N!/(N-n)!n!)$. The difference, $G_{n+1} - G_n = u_0 + k_B T \ln(n/N)$, being the increment of n by 1, is combined with the linear free-energy relationship of the kinetics. The activation energy U_A is given by $U_A = b + u_0 + a k_B T \ln(n/N)$ for constants a and b. The rate of the change $n \rightarrow n+1$ is expressed as $dn/dt = A_1 \exp(-U_A/k_B T)$ for a constant A_1. Elimination of U_A is reduced to $dn/dt = A_2 n^{-a}$. A solution of the differential equation is $n = A_3 t^{1/(a+1)}$. This is the power law.

DLC complicated by redox reactions

Electric energy at DLC accompanied by redox reactions, called pseudo-capacitors, has been expected to have an energetic gain exceeding the sum energy of only the DLC and only the redox reaction [1]. This expectation, however, is inconsistent with the classical concept that the observed current should be a simple sum of the capacitive current, I_C, and the Faradaic one, I_F, [12]. Since the two currents are generated at different sites on an electrode in a parallel form, the observed current is
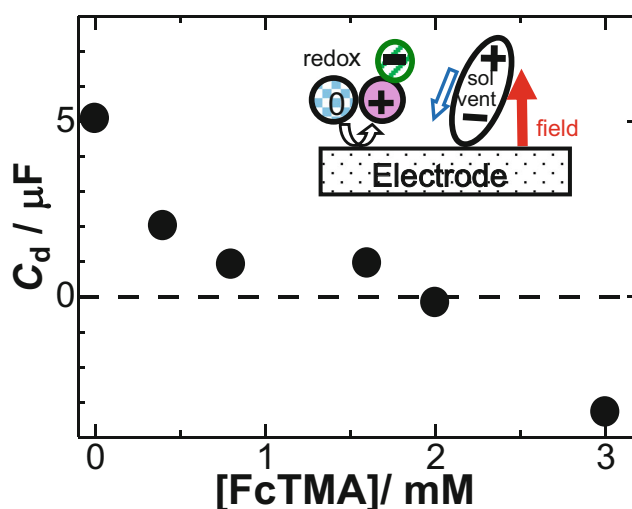
given by $I_P = I_C + I_F$. The parallel occurrence of the DLC and the redox reaction does not support the advantage, $I > I_C + I_F$, of pseudo capacitances.

What happens if I_C and I_F occur at a common site so that they lie in a series in the equivalent circuit? Then the current is given by $I_S = I_C I_F/(I_C + I_F)$, which leads to $I_S < I_C + I_F$ mathematically. This occurs at Frumkin's effect, in which redox reaction rates depend on the DLC structure firmly established with solvents and/or salts. It also occurs when a charge generated by a redox reaction does not relax the applied electric field, in contrary to the DLC by the oriented solvent dipoles, as shown in Fig. 3 [13]. This prediction has been demonstrated to be valid for ac-impedance data by subtracting the imaginary part of the ac-current from the real one to extract only the capacitive component [14]. Then the observed capacitance takes negative values only in the redox potential domain. Even if these techniques are applied to pseudo supercapacitors, $I > I_C + I_F$ would be unexpected. The demonstration of $I > I_C + I_F$ would require to isolate I_C and I_F independently. This may be a big future task to develop pseudo-capacitors.

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