Electrostatic model of solid-state capacitor with ionizable charge traps

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Abstract

We present the analysis of a simple electrostatic model of a solid-state capacitor with ionizable charge traps. It shows a charge-voltage characteristic resembling a chemical battery. With a given withstanding voltage and the same geometry, the energy density of the capacitor with ionizable traps will be lower than that of an ordinary capacitor with metal electrodes.

There is considerable confusion in the industrial sector on the nature of the nanostructured charge storage devices showing a battery-like discharge characteristic[1], *i.e.*, a sudden decrease in discharge current below a threshold voltage. Similar usages of multi valence transition metal oxide nanostructures[2] and clusters[3] and radical polymers[4] are also being pursued in the field of electrochemical capacitors or batteries to increase the volume capacitance of rechargeable energy storage devices. In order to clarify the important issues on those kinds of devices, we here consider a simple electrostatic model of a capacitor with ionizable charge traps. Since the languages of rechargeable chemical batteries and solid-state charge storage devices are not common, it will be worth presenting a model on a unified platform.

The model is simple: wide-gap semiconductor particles with ionizable charge traps, or multi valence transition metal nanoparticles or clusters are deposited on a metal plate with full coverage and sufficient electric connection to make them function as one electrode of a parallel-plate solid-state capacitor. The device can be an electrochemical capacitor or a pseudo capacitor[5], since the electrochemical double layer can be considered as the dielectric of the solid-state capacitor. The charge trap requires certain energy E_a for accommodating an electron corresponding to negative ionization. The charge can be a hole, but we assume a negative charge here without losing generality. The ionization energy is supplied from the electrostatic potential of the capacitor electrode. We can reasonably assume that the ionization energy can be retrieved at the discharge of the traps. Let us consider the charge-discharge characteristics of this device.

We want to supply a certain voltage to the device and examine the amount of charges stored on the electrode. The voltage supply can be replaced by a large capacitor (C_0) with a voltage V. The amount of charge (number of electrons) N accumulated in the capacitor C_0 is given by

$$eN = C_0 V. \tag{1}$$

We connect this voltage source to the charge storage device (electrostatic capacitance C_1) with the ionizable traps. The charge on C_1 is assumed to be zero at the beginning. We calculate the number of elemental charges (n) transported from voltage source C_0 to the device C_1. The total free energy of the capacitor F, which is equal to the sum of the electrostatic energy of the capacitor and the energy of ionization is given

$$F = \frac{e^2}{2}\frac{(N-n)^2}{C_0} + \frac{e^2}{2}\frac{n^2}{C_1} + nE_a \quad / \tag{2}$$

We want to minimize F using $\partial F/\partial n = 0$:

$$\frac{\partial F}{\partial n} = \frac{e^2(n-N)}{C_0} + \frac{e^2 n}{C_1} + E_a = \frac{e^2(C_0+C_1)}{C_0 C_1}\{n - \frac{1}{C_0+C_1}\left(C_1 N - \frac{C_0 C_1}{e^2}E_a\right)\}$$

follows

$$n = \frac{1}{C_0+C_1}\left(C_1 N - \frac{C_0 C_1}{e^2} E_a\right) \quad . \tag{3}$$

It agrees with the formula of an ordinary capacitor when E_a=0.

We eliminate N using Eqs. (1) and (3). We obtain

$$n = \frac{1}{C_0+C_1}\left(C_1 \frac{C_0 V}{e} - \frac{C_0 C_1}{e^2} E_a\right) = \frac{C_0 C_1}{C_0+C_1}\left(\frac{V}{e} - \frac{E_a}{e^2}\right),$$

from which it follows that, by taking the limit of $C_0 \to \infty$,

$$q \equiv en = C_1\,(V - E_a/e). \tag{4}$$

Figure 1(a) shows the charge - voltage (q- V) plot of eq. (4) with the ionizable traps. It is notable that the voltage between the electrodes will suddenly become zero from a finite value (E_a/e) when the discharge is complete, if we assume a small metallic component of the electrode and a finite internal resistance of the device. In other words, the characteristic of the reported device[1] is reproduced. We added Fig. 1(b) and compared it with the plot of an ordinary capacitor with the same geometry. The energy stored in the device is given by an integral along the q - axis, which is indicated by hatching. A beneficial effect of the ionizable traps does exist if we consider the amount of charges is the figure of merit of the device.

However, it must be noted that the limiting factor of capacitor operation is the withstanding voltage of the dielectric between two electrodes. The situation is similar to that in electrochemical capacitors that utilize an electronic double layer; in that case, the withstanding voltage is determined by the potential window of the electrolyte-electrode system. Let us compare the energy that can be stored in the device with a given withstanding voltage V_0 with the same electrostatic capacitance C_1, *i.e.,* with the same geometry of the device. The ordinary capacitor with a metal electrode can store energy

$$E=(1/2)\ C_1 V_0^2 . \tag{5}$$

On the other hand, the capacitor with ionizable traps can store energy

$$E=(1/2) C_1 (V_0^2-(E_a/\mathrm{e})^2) , \tag{6}$$

which can be obtained by using $q=C_1(V_0-E_a/\mathrm{e})$. By comparing Eqs. (5) and (6), we can conclude that the stored maximum energy will decrease when we use the capacitor with ionizable traps. We have considered positive E_a so far, but even if we use negative E_a, *i.e.*, a device with charges already accumulated on the electrode at zero voltage, the stored energy is also lower than that of an ordinary capacitor.

From the above discussion, the effect of the ionizable traps in the reported device must be sought in the function to prevent leakage in the nanostructured electrode-insulator-electrode assembly, for example, by repulsion of the mobile carriers by trapped charges. In the case of electrochemical capacitors, the role of transition metal oxide clusters will be different. They will be effective in increasing the surface area of the electrodes without aggregation and/or in preventing the electrochemical reactions, which are severe problems when nanostructured metal is used as the electrodes and catalysts[6].

In conclusion, we used a simple model and some arithmetic to derive the behavior of the energy storage device that reproduces the battery-like discharge characteristics as reported. We estimated the stored energy with a given withstanding voltage and found that the ionizable traps will decrease the maximum energy density.

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References

1. T. Kudoh, A. Nakazawa, and N. Terakado, Japan Patent 5508542 (2014).

2. T. Brezesinski, J. Wang, S. H. Tolbert, and B. Dunn, Nat. Mater. **9**, 146 (2010).

3. N. Kawasaki, H. Wang, R. Nakanishi, S. Hamanaka, R. Kitaura, H. Shinohara, T. Yokoyama, H. Yoshikawa, and K. Awaga, Angew. Chem., Int. Ed. **50**, 3471 (2011).

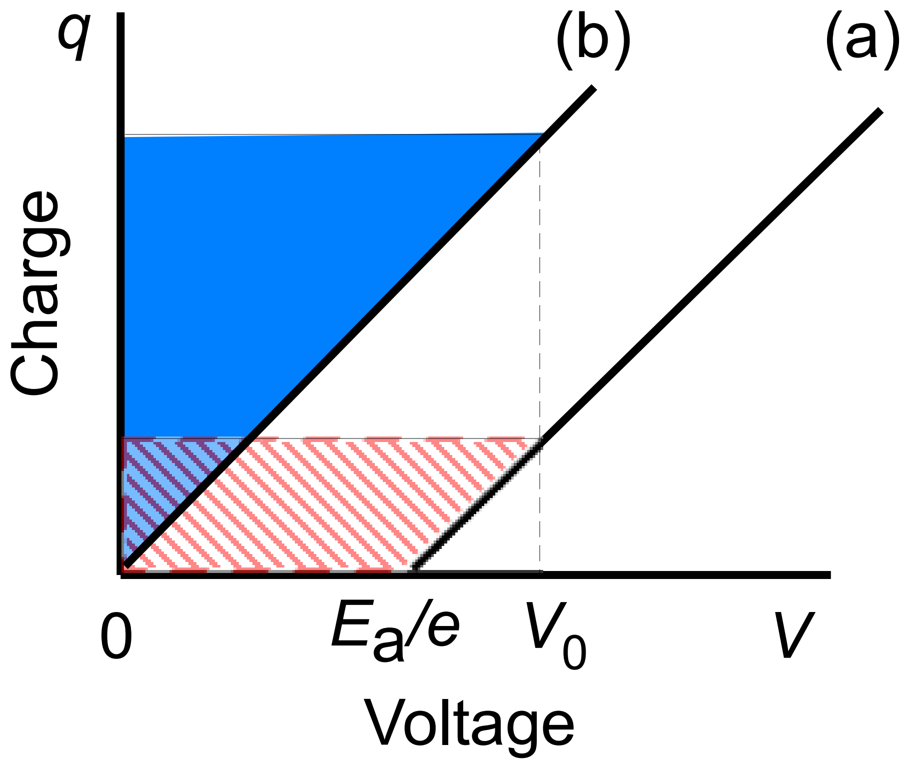
4. T. Janoschka, M. D. Hager, and U.S. Schubert, Adv. Mater. **24**, 6397 (2012).

5. P. Simon and Y. Gogotsi, Nat. Mater. **7**, 845 (2008).

6. S. Mandal, M. Sathish, G. Saravanan, K. K. R. Datta, Q. Ji, J. P. Hill, H. Abe, I. Honma, and K. Ariga, J. Am. Chem. Soc. **132**, 14415 (2010).

Figure Caption

Fig. 1. (Color online) Charge-voltage characteristic of capacitors (a) with and (b) without ionizable traps.



q
Charge
(b)
(a)
0
Ea/e
V0
V
Voltage