AC impedance spectra of activated carbon at charged states -Effect of pore size and ion size

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Electric double-layer capacitors, which are in commercial –ized state, use activated carbon as active material. Activated carbon has many pores, especially micropores, and they contribute large surface area of activated carbon. Many researchers think that radius of micropore is smaller than thickness of electric double layer formed on the surface of electrode and therefore micropore cannot contribute energy storage by electric double-layer.(1)Impedance spectroscopy can show physical properties and chemical reactions of electrodes. Therefore, some researchers used impedance analysis for knowing the role of micropores in EDLC. But most of them are measured at uncharged states. Real capacitors carry out their roles at charged states. So it needs to check the behavior at charged states. In this experiment, we chose two activated carbon – A : microporous and B : mesoporous. And we measured impedance behaviors at charged states. Table 1 shows the physical properties of activated carbon.

Table 1. Physical properties of activated carbon

Properties	A	B
Specific Surface Area (m^2/g)	1748	2457
Mesopore Area (m^2/g)	171	1112
Mesopore to total area ratio (%)	11	45
Mesopore to total volume ratio (%)	16	59
Average pore size (nm)	1.91	2.08
Capacitance (F/g) Measured in 1M Et_4NBF_4/Propylene carbonate	108	140

We observed impedance behaviors of A and B at various charged state. Working electrodes were made by slurry-coating on the aluminum foil. Carboxymethylcellulose was used as binders. Electrolyte was 1M Et_4NBF_4 /Propylene carbonate(PC) and reference electrode was lithium metal. Open-circuit potential (OCP) of A and B carbon is 3.1V vs. Li. If the potential of working electrode is lower than 3.1V vs. Li, the electrode is in negatively charged state and the larger is the gap between the potential of working electrode and OCP, the more negatively charged state is.

(a) A carbon (b) B carbon

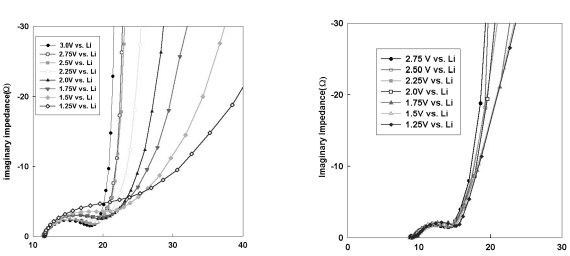

Fig. 1. Nyquist plot of A and B carbon at negatively charged state

Fig. 1 is Nyquist plot of A and B carbon at negatively charged states. In general, a polarized electrode is represented by constant phase element (CPE). In ideal case, the phase of polarized electrode is 90^o. In Fig 1., the Nyquist plot shows that activated carbon electrode is represented as combination of the solution resistance, contact resistance and constant phase element. At B carbon, as potential is charged negatively, the angle of CPE part is almost invariable. But at A carbon, the angle of CPE part decreases, as potential is charged negatively. A and B carbon shows no evident Faradaic reaction at measured potentials. So the reason of it is caused by the difference of physical properties between A and B carbon. To make sure that this effect is caused by the difference of pore size, we used smaller ions than tetraethylammonium ion such as Ethyltrimethylammonium ion($EtMe_3N^+$).

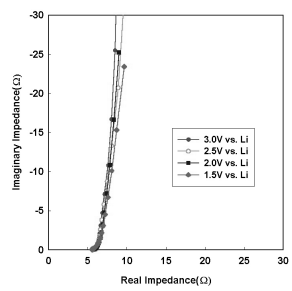

Fig. 2. Nyquist plot of A carbon in 1M $EtMe_3NBF_4$/Propylene carbonate

Fig. 2 shows the Nyquist plot measured in 1M $EtMe_3N$ BF_4/Propylene carbonate using A carbon. Contrary to Fig. 1(measured in Et_4NBF_4/Propylene carbonate), this graph shows no change of angle of CPE part. Smaller ions in a pore may have the same meaning of the increase of pore radius. Therefore, the result of Fig. 2 suggests that the change of angle of CPE is caused by the pore size.
It is known that the size of ethyltrimethylammonium ion in PC is 0.298 nm and that of tetraethylammonium in PC is 0.343nm.(2) Comparing Fig. 1(a) with Fig. 2, it can be postulated that CPE angle begins to change at a critical ratio of ion size and pore size.
From these data, the electrolyte in micropores at charged states has other properties than the electrolyte in mesopores. Recently, it is suggested that the variation of resistance in electrode or electrolyte can give rise to non-ideal capacitor behavior. (3)
These phenomena can give important effects to EDLC performance. Because the using condition of EDLC is not OCP state but charged state, non-ideal capacitive behavior such as small CPE angle affect the discharging properties of EDLC, especially high power charging/discharging condition. (4)

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Reference

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