

Short communication

# Activation of an ionic liquid electrolyte for electric double layer capacitors by addition of BaTiO<sub>3</sub> to carbon electrodes

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## Abstract

To increase the capacitance of an electric double layer capacitor (EDLC) containing 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF<sub>4</sub>) as an ionic liquid electrolyte, barium titanium oxide (BaTiO<sub>3</sub>) as a ferroelectric material is incorporated into activated carbon electrodes. An EDLC composed of BaTiO<sub>3</sub> powder/activated carbon composite electrodes and the ionic liquid electrolyte EMIBF<sub>4</sub> exhibits a large capacitance when compared to the corresponding EDLC without BaTiO<sub>3</sub>. Moreover, the rate performance of the EDLC containing BaTiO<sub>3</sub> is improved when the electrodes are prepared by an improved method, i.e., vacuum penetration of BaTiO<sub>3</sub>-dispersed EMIBF<sub>4</sub> into the activated carbon electrodes. No positive addition effect of BaTiO<sub>3</sub> is observed for the corresponding EDLC with a typical organic electrolyte composed of a tetraalkylammonium salt and propylene carbonate as a solvent. These results suggest that BaTiO<sub>3</sub> incorporated into the electrodes would improve the dissociation of the ionic liquid EMIBF<sub>4</sub>, and hence increase the carrier concentration available for the formation of an electric double layer.

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**Keywords:** Electric double layer capacitor; Ionic liquid electrolyte; Capacitance; Ionic dissociation; Composite electrode

## 1. Introduction

An electric double layer capacitor (EDLC) is an attractive power storage device because of its rapid charge–discharge performance and long cycle life when compared to those of common secondary batteries. While an EDLC should be a suitable rechargeable power source for a fast-response uninterruptible power supply (UPS) as well as a regenerative brake system for vehicles, it has so far been regarded as unsuitable for a driving power source because of its low energy density. Continuous efforts have, therefore, been devoted to developing a novel EDLC with a high energy density applicable to large-scale devices by improving its electrode as well as electrolyte material.

Generally, EDLC electrolytes are classified into organic and aqueous solutions. Although an aqueous electrolyte for EDLCs shows high ionic conductivity and can provide excellent safety, its working voltage is limited by the electrolysis voltage of water: below ca. 1.2 V. This means that the energy density of an aqueous EDLC should be lower than that of an organic one. Recently, considerable attention has been focused on an ionic liquid as an alternative electrolyte material, because an ionic liquid has a wide electrochemical window compared to that of an aqueous solution, an extremely low vapor pressure, and incombustibility. An ionic liquid is essentially composed only of ionic species, i.e., cations and anions, without any solvent. Some fraction of the ions in the liquid contributes to ionic conduction without an additional electrolytic salt. The application of an ionic liquid electrolyte can, therefore, provide both safety and a high energy density (a high operating voltage) for an EDLC [1–5].

Such advantages of an ionic liquid would provide an optimistic outlook for its application to an advanced EDLC electrolyte. The actual degree of dissociation of an ionic liquid is, however, widely known to be insufficient for a practical EDLC electrolyte, although there have been somewhat overestimated

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values of the dissociation degree, which were calculated on the theoretical basis of impedance response as well as nuclear magnetic resonance (NMR) for ionic liquids [6–9]. The limitation of dissociation is derived mainly from a strong electrostatic binding directly between ions without solvation (due to the absence of any solvent). In contrast, dissolved salts are effectively dissociated by solvation in a conventional electrolyte; the resulting solvated ions are essentially active.

In this context, a low concentration of mobile carriers in an ionic liquid would lead to not only a high internal cell resistance but also a poor capacitance of EDLCs due to an insufficient amount of adsorptive ions. Thus, we should improve the inefficient dissociation to enhance the capacitance of EDLC. A common strategy for doing so is to add a reasonable amount of high-permittivity organic solvent to the defective electrolyte so that ion solvation can effectively occur. The addition of flammable organic solvents might, however, spoil a unique advantage of ionic liquids, i.e., their incombustibility consistent with a high withstand voltage. In our opinion, therefore, the addition of the solvents is not a decisive way to improve the properties of an ionic liquid electrolyte, although we sometimes perform this by necessity.

Such an ionic association problem in regard to enhancing carrier concentration has been discussed also for lithium polymer batteries based on representatively polyethylene oxide (PEO) electrolytes. There, lithium cations are trapped by oxygen atoms in the polymer chains, hence the lithium carrier concentration would not be enough even though the oxygen coordination with lithium could induce the dissociation of lithium salts. In an attempt to solve this problem in lithium batteries, the addition of ceramic material as filler in the polymer has been reported: a remarkable improvement in lithium ion conductivity was observed for the polymer electrolyte when a ferroelectric material, barium titanium oxide  $\text{BaTiO}_3$ , was used as filler [10–14]. This improvement would correlate with an effect of the polarized  $\text{BaTiO}_3$  particles on the dissociation of lithium ions.

The results also suggest that such a concept could be applied to another controversial electrolyte system to be improved, an ionic liquid electrolyte for EDLCs. Our methodology in this work is to use a carbon composite electrode containing ferroelectric  $\text{BaTiO}_3$  powders in an attempt to improve the dissociation of an ionic liquid effectively inside or in the vicinity of the electrode, leading to the increase of double-layer electrode capacitance. To establish our idea herein we prepared the  $\text{BaTiO}_3$ -containing activated carbon electrodes and examined the electrochemical behavior of those electrodes in a typical ionic liquid electrolyte for EDLCs.

## 2. Experimental

An activated carbon sheet electrode (Japan Gore-tex, 400  $\mu\text{m}$  thick, carbon 85%) was cut into a disk shape ( $10\phi$ ) and attached to a piece of aluminum (Al) foil of the same size with a conductive paint (Nippon Graphite Industries Co., Varniphite). The layered electrode composed of the activated carbon sheet and Al foil was dried at 150  $^\circ\text{C}$  for 24 h.

$\text{BaTiO}_3$  composite electrodes were obtained by the following different methods. Method (i):  $\text{BaTiO}_3$  powder (Kishida Chemical Co., ca. 1  $\mu\text{m}$ , 99.98% purity, 0.01 g) was spread on the surface of as-prepared activated carbon electrodes and then pressed; method (ii): the powder (0.02 g) was mixed with the conductive paint and coated onto the Al foil before attaching the activated carbon sheet to it; method (iii): the powder (0.05 g) was dispersed in the electrolyte, after which the electrolyte *in vacuo* penetrated into the as-prepared activated carbon electrodes.

A test EDLC was assembled from the activated carbon electrodes with and without  $\text{BaTiO}_3$  and a 13- $\phi$  paper separator (Nippon Kodoshi Co, TF4035) in a Teflon housing. An ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF<sub>4</sub>, Sanyo Chemical Industries, 170-ppm H<sub>2</sub>O) was used as an electrolyte because of its high conductivity and low viscosity when compared to other conventional ionic liquids [15,16]. An organic electrolyte, 1.96 M triethylmethylammonium tetrafluoroborate/propylene carbonate (TEMABF<sub>4</sub>/PC, Tomiyama Pure Chemical Industries) was also used for evaluating the performance of the  $\text{BaTiO}_3$ -composite electrodes in a typical solvent-containing electrolyte system for EDLCs.

The electrochemical properties were estimated using a constant-current charge–discharge technique (Hokuto Denko, HJ1001SM8). The discharge capacitances at various current densities were calculated from passed electricity and a working voltage range, where any voltage loss due to IR drop was eliminated from a preset voltage range of 1–2.5 V. The EDLCs were galvanostatically charged to 2.5 V and kept there for the measurement of leak currents, and then they were kept under open-circuit conditions for the evaluation of their self-discharge characteristics.

## 3. Results and discussion

Fig. 1 shows the dependence of discharge capacitance on the current density, i.e., rate performance, for the activated car-

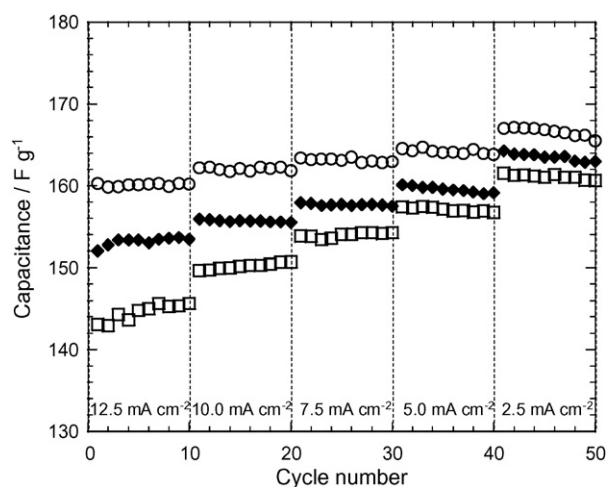


Fig. 1. Dependence of discharge capacitance on current density for  $\text{BaTiO}_3$  composite and as-prepared (normal) activated carbon electrodes in the EMIBF<sub>4</sub> electrolyte: (□) pressed electrode via method (i), (○) coated electrode via method (ii), and (◆) normal electrode.

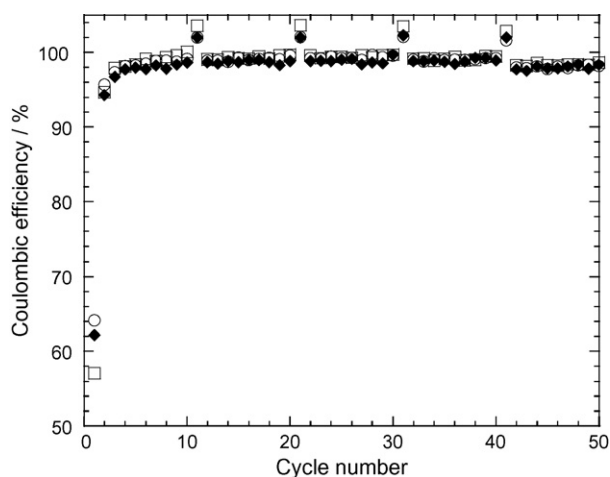


Fig. 2. Relationship between charge–discharge coulombic efficiency and cycle number for BaTiO<sub>3</sub> composite and as-prepared (normal) activated carbon electrodes in the EMIBF<sub>4</sub> electrolyte; these values were calculated from the data related to Fig. 1: (□) pressed electrode, (○) coated electrode, and (◆) normal electrode.

bon electrodes with and without BaTiO<sub>3</sub> in the ionic liquid electrolyte, EMIBF<sub>4</sub>. The “normal” activated carbon (without BaTiO<sub>3</sub>) electrode indicated capacitances of 152–164 F g<sup>-1</sup> at the applied rates from 12.5 to 2.5 mA cm<sup>-2</sup>. According to previous reports on the prototype EDLCs containing activated carbon with a large specific surface area (>2000 m<sup>2</sup> g<sup>-1</sup>) [17,18] as an electrode material and EMIBF<sub>4</sub> as an ionic liquid electrolyte, the reported capacitances were 120–180 F g<sup>-1</sup>, which are close to the present results [13,14]. While the BaTiO<sub>3</sub> composite electrode prepared by pressurization (method (i)) showed rather lower capacitances than the normal electrode, another composite electrode prepared by method (ii) exhibited larger capacitances at any applied rate than the electrode by the pressing method (i) as well as the normal electrode.

Detachment of BaTiO<sub>3</sub> particles from the electrode surface and hindrance caused by the detached BaTiO<sub>3</sub> were confirmed as origins of the capacitance decrease of the composite electrode prepared using method (i). Although a higher pressure than we applied could seemingly stabilize the composite electrode, the high stacking force actually led to the destruction of activated carbon – especially its pore structure directly as well as indirectly – by BaTiO<sub>3</sub> particles, which are much harder than activated carbon. In contrast, the coating method with a conductive paint containing BaTiO<sub>3</sub> (method (ii)) would effectively dissociate the ionic liquid and thus contribute to an increase in electric double layer capacitance without detachment of BaTiO<sub>3</sub> particles as well as degradation of activated carbon. Fig. 2 shows coulombic efficiencies corresponding to the data in Fig. 1. There is no apparent electrochemical degradation such as a redox side reaction even in the presence of BaTiO<sub>3</sub>.

As mentioned above, the addition of BaTiO<sub>3</sub> in an appropriate way to activated carbon electrodes was found to enhance the capacitance, conceivably originating from facilitating ionic dissociation of the ionic liquid EMIBF<sub>4</sub>. The coating method (method (ii)) improved the capacitance, whereas the pressing method (method (i)) diminished the double layer capacitance.

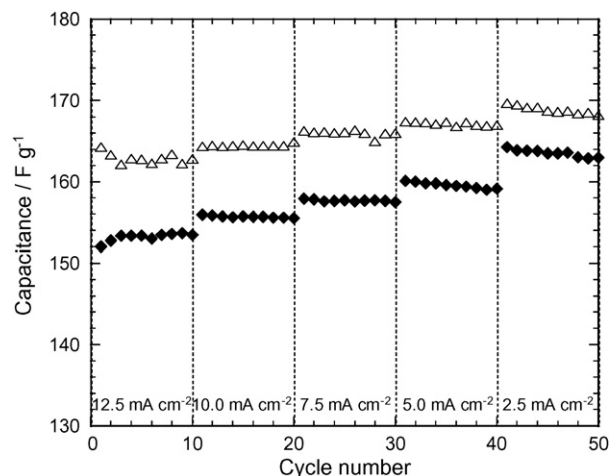


Fig. 3. Dependence of discharge capacitance on current density for an improved BaTiO<sub>3</sub> composite and as-prepared (normal) activated carbon electrodes in the EMIBF<sub>4</sub> electrolyte: (Δ) VP electrode prepared by the vacuum penetration method (iii) and (◆) normal electrode.

These results suggest that the way electrodes are hybridized with BaTiO<sub>3</sub> governs the capacitance and that there would remain scope for further modification. Generally, electric double-layer capacitance depends on the available surface area of activated carbon. Therefore, we must avoid introducing a hybridization technique such as method (i) that causes excessive BaTiO<sub>3</sub> localization, which reduces the available surface area of carbonaceous electrode material. A desirable technique should be a fine hybridization that provides uniform dispersion of BaTiO<sub>3</sub> in the sheet electrode overall. Thus, we tried to apply the following vacuum penetration method as a modified hybridization technique (method (iii)) to the activated carbon electrodes in the ionic liquid electrolyte; BaTiO<sub>3</sub> was dispersed in EMIBF<sub>4</sub>, after which the resulting liquid *in vacuo* penetrated into the as-prepared activated carbon electrodes.

Fig. 3 shows the discharge capacitances of the composite electrodes by method (iii), “VP electrode,” in the ionic liquid. These capacitances at any rate are obviously higher than those of the normal electrode. Furthermore, judging from the comparison of the respective rate capability between Figs. 1 and 3, the electrode made by method (iii) seems to somewhat surpass the coated electrode made by method (ii) in the observed capacitance at any rate. We attributed these results to the efficient ionic dissociation induced by the uniform, three-dimensional dispersion of BaTiO<sub>3</sub> particles inside the carbon sheet, which was difficult to achieve by the pressing and coating methods.

Here one should consider the possibility that increasing capacitance for those composite electrodes might be caused by some Faradaic reactions of EMIBF<sub>4</sub> with the BaTiO<sub>3</sub> particles. To investigate this, EDLC cells with the various electrodes were kept at a charged voltage of 2.5 V and their leak currents were monitored as a function of duration. Every EDLC showed an essentially similar current–time profile irrespective of the presence of BaTiO<sub>3</sub>. We can conclude, therefore, that BaTiO<sub>3</sub> is electrochemically robust against the ionic liquid and thus does not cause ionic liquid degradation that hinders EDLC performance.

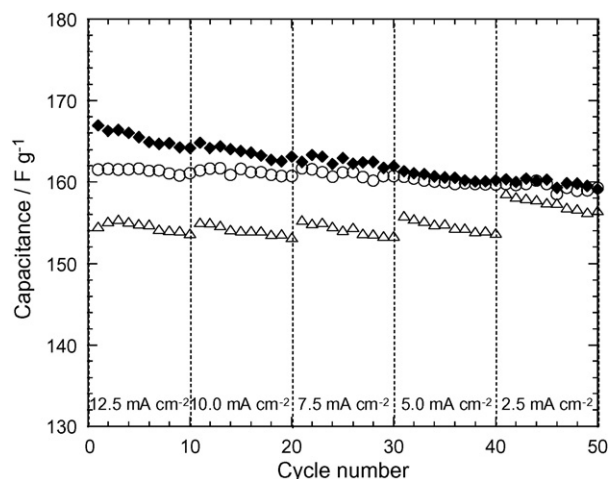


Fig. 4. Dependence of discharge capacitance on current density for BaTiO<sub>3</sub> composite and as-prepared (normal) activated carbon electrodes in TEMABF<sub>4</sub>/PC as a typical solvent electrolyte: (Δ) VP electrode, (○) pressed electrode, and (◆) normal electrode.

It is widely known that the degree of ionic dissociation of an electrolytic salt in an organic solvent electrolyte for a conventional EDLC is much higher than that of an ionic liquid in the absence of any solvent. When the BaTiO<sub>3</sub> composite electrodes are applied to a typical organic electrolyte, therefore, one can expect that there is no or little increase in capacitance. To elucidate this, the composite electrodes were also applied to TEMABF<sub>4</sub>/PC, which is a typical organic electrolyte for EDLC. Fig. 4 shows the rate performance of BaTiO<sub>3</sub> composite activated carbon electrodes in the TEMABF<sub>4</sub>/PC electrolyte, together with the performance of a normal electrode. Discharge capacitances of the composite electrodes were rather lower than that of the normal electrode in the organic electrolyte. This suggests that BaTiO<sub>3</sub> can act as a dissociation enhancer only for an ionic liquid whose ionic dissociation is inherently insufficient. Rather, for the organic electrolyte the BaTiO<sub>3</sub> particles would hinder the access of carrier ions to the activated carbon surface. Thus, the addition effect of BaTiO<sub>3</sub> may essentially consist of competitive factors, i.e., a dissociation enhancer as a positive function as well as an electrode inhibitor as a negative influence. In ionic liquid electrolytes such as EMIBF<sub>4</sub> with a poor ionic dissociation, the positive effect is sometimes dominant, although the observed effect depends on the hybridization methods (i)–(iii). In common solvent electrolytes with a sufficient dissociation, however, there is little scope for improving dissociation by BaTiO<sub>3</sub>; only observed is a negative inhibiting effect of BaTiO<sub>3</sub> addition.

#### 4. Conclusions

The ferroelectric material BaTiO<sub>3</sub> was incorporated into activated carbon electrodes by several methods in an attempt to increase their discharge capacitance in the ionic liquid elec-

trolyte EMIBF<sub>4</sub>. The best hybridization technique to improve the capacitance was the vacuum penetration of EMIBF<sub>4</sub>, containing dispersed BaTiO<sub>3</sub> powder, into the activated carbon electrodes. The obvious, positive incorporation effect of BaTiO<sub>3</sub> would appear especially when ions dissociated by BaTiO<sub>3</sub> were distributed widely through the electrode; i.e., when the three-component interface of carbon/BaTiO<sub>3</sub>/ionic liquid was effectively formed in the electrodes. Our future research, focusing on the optimum particle size and addition amount of BaTiO<sub>3</sub>, will be carried out with the aim of further increasing the ionic liquid EDLC capacitance.

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