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ABSTRACT

Hard carbon is widely studied as a promising negative electrode in sodium-ion batteries. To achieve its stable charge-discharge reaction, a fluorine-rich passivation film arising from a fluorinated salt or solvent in an electrolyte was demonstrated to be effective, but its essential role remained unclear. Here, we report a sodium tetraphenylborate (NaBPh4)/1,2-dimethoxyethane (DME) electrolyte that is free from fluorine but enables the highly stable and high-rate charge-discharge cycling of hard carbon electrodes as compared to other combinations of Na salts and solvents. Surface analysis of the cycled electrode shows that the NaBPh4 is not decomposed during the cycle and that solid electrolyte interphase (SEI) is derived from DME. Hence, fluorine-based components are not indispensable to stabilize the hard carbon/electrolyte interface. The DME-derived SEI, though containing no F component, can highly stabilize the interface to enable the reversible and high-rate cycling of hard carbon.

Keywords: Sodium-ion Batteries, Hard Carbon, Electrolyte, Fluorine

1. Introduction

With growing concern about the supply risk of lithium resources, sodium-ion batteries (NIBs or SIBs) using abundant and low-cost sodium resources are actively researched for large-scale energy storage.1-5 Hard carbon is a promising negative electrode for NIBs owing to its large capacity (>250 mAh g⁻¹) and low reaction potential (<0.1 V versus Na⁺/Na⁻).6-9 The potential profile of hard carbon upon sodiation is composed of a sloping region (0.1 V–2.5 V) and a plateau region (0 V–0.1 V), and the latter constitutes more than half of the overall capacity. Because of this low reaction potential, at which most organic compounds are reduced, selecting additives) or functional binders is essential to achieve the reversible cycling of hard carbon electrodes.5,10-14

Regarding the electrolyte design, a solid electrolyte interphase (SEI),15,16 which is formed on a negative electrode by sacrificial reductive decomposition of electrolyte components, dominates the reversibility and kinetics of sodium insertion into hard carbon electrodes. Recent studies showed that a stable SEI could be formed by using fluorinated electrolytes containing, for example, sodium hexafluorophosphate (NaPF₆),11,17 sodium bis([fluorosulfonyl])amide (NaFSA),18-20 and fluoroethylene carbonate (FEC).21-23 These fluorinated compounds are decomposed on the electrode surface to produce NaF, which has low solubility in an aprotic solvent, thus being considered to function as an essential component of the SEI to effectively suppress electrolyte decompositions. However, from the viewpoint of green chemistry, the use of these fluorinated compounds is unfavorable due to their high toxicity and high environmental load. Because of this, fluorine-free electrolytes are being studied extensively.24,25

Recently, our group reported a fluorine-free electrolyte composed of sodium tetraphenylborate (NaBPh4, Fig. 1a) and 1,2-dimethoxyethane (DME) that enables highly reversible plating/stripping of sodium metal negative electrodes.26 This electrolyte does not contain fluorine, phosphorus, or sulfur element, thus, there is no risk of generating a toxic gas (e.g., hydrogen fluoride (HF), phosphoryl fluoride (POF₃), phosphorus pentfluoride (PF₅), or sulfur dioxide (SO₂)).27-30 More importantly, this work suggests that fluorine is not indispensable in stabilizing such low-potential negative electrodes, although the detailed mechanism of the interface stabilization is still unclear.

In this work, we studied the electrochemical reaction of hard carbon negative electrodes in a fluorine-free NaBPh4/DME electrolyte. To understand the mechanism of stabilizing the interface, we scrutinized the effects of both counter anions and solvents using various salt/solvent combinations. We found highly reversible and high-rate cycling of hard carbon negative electrodes in NaBPh₄/DME electrolyte, suggesting that fluorine species are not indispensable in stabilizing the hard carbon/electrolyte interface. The mechanism of stabilizing the interface in this electrolyte was discussed based on the analysis of the electrode surface.

2. Experimental

2.1 Preparation of electrolytes

NaBPh₄ (99.5%) was purchased from Wako Pure Chemical Industries. Sodium bis(trifluoromethanesulfonyl)amide (Na(N(SO₂CF₃)₂), NaTFSA), NaPF₆, ethylene carbonate (EC)-diethyl carbonate (DEC) (1:1 by volume), sulfolane (SL), DME, dimethyl carbonate (DMC), and a conventional electrolyte of 1 mol dm⁻³ (M) NaPF₆ in EC:DEC (1:1 by volume) were provided by Kishida Chemical and were of battery grade. High-purity NaFSA was supplied by Nippon Shokubai. NaBPh₄ was dried under vacuum at 120°C for 12 h and the other battery-grade materials were used without any pretreatment. To prepare electrolyte solutions, Na salts were dissolved in solvents under Ar atmosphere in a glove box (Miwaco Inc., Japan).
2.2 Electrochemical measurements

Hard carbon (Carbotron P(J) provided by Kureha was used as a negative electrode without any further purification. The hard carbon was mixed with carboxymethyl cellulose (CMC2200, Daicel) as a binder at a weight ratio of 9:1 in deionized water. The slurry was pasted onto copper current collector (thickness: 10 µm, Fuchikawa Material) with a doctor blade and then dried at 60°C. Na$_2$V$_3$O$_7$ was synthesized as reported in previous works. The Na$_2$V$_3$O$_7$ electrode sheet was prepared by pasting a slurry made of Na$_2$V$_3$O$_7$ (80 wt%) mixed with Ketjen black (10 wt%, KB, Lion Corp.) and polyvinylidene fluoride (10 wt%, PVdF, Kureha) in N-methylpyrrolidone (NMP, Wako) onto Al foil using a 100 µm doctor blade and then dried at 60°C. The dried electrode sheets were punched into 12 mm diameter pieces and further dried overnight at 150°C (for hard carbon) or 120°C (for Na$_2$V$_3$O$_7$) in a vacuum. The mass loading of the negative electrode was ca. 1.6 mg cm$^{-2}$.

For battery tests, coin cells (2032 type) were assembled under Ar atmosphere in a glovebox (Miwa Inc.). A Na metal (Wako) counter electrode and a glass fiber separator (GB-50, Advantec) were used. The assembled hard carbon | Na metal and Na$_2$V$_3$O$_7$ | Na metal coin cells were subjected to charge-discharge tests at 25°C with HJ1001SD8 (Hokuto Denko) at current densities of 20 mA g$^{-1}$. The mass capacity was determined from charge/discharge cycles.

2.3 Characterization of electrolytes and SEI

The X-ray photoelectron spectroscopy (XPS) was applied to examine the surface of hard carbon electrodes. A PHI 5000 VersaProbe II spectrometer (ULVAC-PHI, Inc.) with Al K$_\alpha$ radiation was used. Before the XPS measurement, the hard carbon electrodes were subjected to three-cycles charge-discharge measurement at 20 mA g$^{-1}$. Then, the hard carbon electrodes were recovered from the cells under Ar atmosphere, washed with DMC, and dried in a vacuum. A transfer vessel was used to transfer the electrodes into the XPS chamber without any contamination from air.

3. Results and Discussion

3.1 Physicochemical properties

Figure 1b shows the ionic conductivities of NaBPh$_4$/DME and NaPF$_6$/DME. At a low concentration of <0.4 M, the ionic conductivity of NaBPh$_4$/DME was higher than that of NaPF$_6$/DME, suggesting the inherent high degree of dissociation for NaBPh$_4$ salt. With increasing concentration to above 0.4 M, the ionic conductivity of NaBPh$_4$/DME became lower than that of NaPF$_6$/DME because of the bulky BPh$_4^-$ anion that leads to a short cation-anion mean distance, promoting ionic association. The NaBPh$_4$/DME exhibited a maximum ionic conductivity of 6.3 mS cm$^{-1}$ at 0.5 M, which is comparable to those of 0.5 M NaPF$_6$/DME (8.1 mS cm$^{-1}$) and 1 M NaPF$_6$/EC:DEC (9.0 mS cm$^{-1}$). On this basis, we chose the concentration of 0.5 M for NaBPh$_4$/DME in the following experiments.

3.2 Electrochemical stability

To study the cathodic and anodic stability of 0.5 M NaBPh$_4$/DME, CV and LSV tests were conducted on Cu and Pt electrodes, respectively (Fig. 1c). For the cathodic side, this electrolyte enabled reversible plating/stripping of sodium metal. The seemingly low reversibility as compared with a previous report was caused by the separator-less three-electrode cell configuration, in which the plated sodium metal is not subjected to external pressure. Small reduction current was observed below 0.8 V (vs. Na$^+$/Na) only in the first cycle, which might have resulted from the formation of SEI or the decomposition of contaminants in the electrolyte or on the electrode. On the other hand, the anodic limit of 0.5 M NaBPh$_4$/DME was ca. 3.4 V (vs. Na$^+$/Na). Although this anodic limit is not high compared with conventional electrolytes (~4 V), the electrolyte also enabled the highly reversible charge-discharge reaction of a positive electrode (Na$_2$V$_3$O$_7$) with higher rate capability than 1 M NaPF$_6$/EC:DEC (1:1 by volume) (Fig. S1).

3.3 Effect of Na salt on the cycling stability of hard carbon

First, we studied the charge-discharge cycling performance of hard carbon half cells using various Na salts in combination with reduction-tolerant DME solvent (Fig. 2). The results are also summarized in Table 1. Notably, the 0.5 M NaBPh$_4$/DME electro-
lyte exhibited the highest initial Coulombic efficiency of 95.0% with high capacity retention of 95.6% over 100 cycles, suggesting the minimized reductive decomposition of the electrolyte components for forming a stable SEI. Besides, the capacity of the plateau region close to 0 V was even larger than in 1 M NaPF₆/EC:DEC owing to the decreased polarization; hence, the formed interface has lower resistance. As for other salts, 0.5 M NaPF₆/DME exhibited high capacity retention of 95.7% during 100 cycles, but the average Coulombic efficiency during cycles was low (ca. 98.5%), indicating that the SEI is less stable than that with NaBPh₄/DME.

When 0.5 M NaFSA/DME and 0.5 M NaTFSA/DME were used, the charge-discharge reactions were unstable and less reversible, suggesting that these electrolytes could not form a stable interface. In NaFSA/DME, reversible sodiation/desodiation basically proceeded, but sometimes its voltage abruptly dropped during desodiation and did not reach the upper cut-off; this behavior is characteristic of some shuttling reactions between the electrodes arising from the unstable interfaces (Fig. S2). In NaTFSA/DME, the reversible capacity was rapidly decreased during initial several cycles. In the cycled cell, the color of the Na metal and the separator was changed to yellow, suggesting extensive electrolyte decompositions at the Na metal as well as the hard carbon. On this basis, the counter anions of sodium salts dominate the interfacial stability of such low-potential electrodes; importantly, the presence of fluorine species is not a sufficient condition for stabilizing the interface.

3.4 Effect of solvent on the reaction kinetics of hard carbon

Having found the high stability of NaBPh₄ salt, we next tested hard carbon half cells using various electrolyte solvents with a focus on the reaction kinetics (Fig. 3). Notably, 0.5 M NaBPh₄/DME could retain a high reversible capacity of over 200 mA h g⁻¹ even at...
6000 mA g⁻¹ owing to low polarization (Fig. 3ab), which is distinct from the almost zero capacity in conventional 1 M NaPF₆/EC:DEC.

Besides, high capacity retention of over 82% was observed after 1500 cycles at a current density of 1000 mA g⁻¹ (Fig. 3c). As for other solvents, a similar high-rate character was also observed in 0.5 M NaBPh₄/THF, whereas much poorer kinetics were observed for 0.5 M NaBPh₄/EC:DEC and SL, suggesting that the selection of ether solvents is effective for achieving high-rate performance.

To confirm that the high rate performance resulted from the hard carbon electrodes, we conducted an AC impedance measurement for hard carbon | hard carbon symmetric cells with various electrolytes. The hard carbon electrodes were charged in advance to 0.01 V in a half cell. As shown in Fig. 4, the symmetric cells exhibit a small Z' intercept and two semicircles at high and middle-to-low frequency regions. An equivalent circuit corresponding to this system is shown in the inset. The Z' intercept is ascribed to the sum of the solution resistance of the electrolyte (Rₛ) and the electronic resistance of the electrodes (Rₑ). The semicircles at high and middle-to-low frequency regions correspond to the resistance in SEI (Rₓe) and the charge-transfer resistance (Rₓt), respectively. Notably, 0.5 M NaBPh₄/DME electrolyte resulted in smaller Rₓt than 0.5 M NaBPh₄/EC:DEC. Hence, the observed high rate performance of the hard carbon half cell with 0.5 M NaBPh₄/DME did arise from low Rₓt at the hard carbon/electrolyte interface. Based on this result, the combination of NaBPh₄ with ether solvents such as DME is essential for forming a stable and low-resistance interface.

3.5 Interphasial chemistry

For further insights into the stable and low-resistance interface, the interphasial chemistry on the cycled hard carbon was investigated via XPS (Fig. 5). On the hard carbon cycled in 1 M NaPF₆/EC:DEC or 0.5 M NaTfSA/DME electrolytes, NaF was detected as an SEI component. Moreover, sulfides were formed as an SEI component in 0.5 M NaTfSA/DME. These results suggest

![Figure 3](image3.png)

**Figure 3.** (a) Charge-discharge voltage profiles of hard carbon | Na metal half cells with various 0.5 M NaBPh₄ electrolytes as compared with a standard 1 M NaPF₆/EC:DEC (1:1 by volume) at increasing current densities from 20 mA g⁻¹ to 6000 mA g⁻¹. (b) Reversible capacities of the half cells at various current densities. (c) Cycling performances of the half cells at a current density of 1000 mA g⁻¹.

![Figure 4](image4.png)

**Figure 4.** Nyquist plots of hard carbon | hard carbon symmetric cells with 0.5 M NaBPh₄/DME and 0.5 M NaBPh₄/EC:DEC (1:1 by volume). The hard carbon electrodes were in the charged state at 0.01 V. The inset shows an equivalent circuit for this system. The symbols Cₓe and Cₐ denote capacitive elements in the SEI and the electric double layer, respectively.
that NaPF₆ and NaTFSA are decomposed during the cycle to provide some SEI components. However, considering the poor cycling performance in NaTFSA/DME electrolyte, the presence of NaF or sulfides is not a sufficient condition for stabilizing the interface, unless they are formed densely, for example, using concentrated electrolytes. On the other hand, in NaBPh₄/DME electrolyte, only negligible amounts of B compound, as well as F and S compounds, were detected as SEI components. Hence, NaBPh₄ is not decomposed on hard carbon negative electrodes during cycling. Instead, the C1s spectrum changed significantly compared with other electrolytes, suggesting the contribution of DME solvent to forming the SEI, although its detailed composition is not clear at present. This DME-derived SEI, though containing no F component, can stabilize the interface in NaBPh₄/DME electrolyte, thus leading to the stable cycling of hard carbon electrodes.

As shown previously, the DME-derived SEI, composed of carbon, oxygen, and sodium elements, is thin, stable, and highly Na⁺-conductive. Hence, it does not need any other component from counter anions for stabilizing the interface. More preferably, the counter anions should be highly tolerant of reductive decomposition, possibly even at the low reaction potential (~0 V vs. Na⁺/Na) of hard carbon electrodes to minimize the loss of Coulombic efficiency. From this perspective, BPh₄⁻ anion has a remarkably lower electron affinity than other anions, and is thus more tolerant to reduction. Hence, among the several sodium salts studied, NaBPh₄ is the most favorable for use in combination with DME that enables the highly stable and high-rate cycling of such low-potential negative electrodes.

4. Conclusion

The highly reversible and high-rate charge-discharge cycling of hard carbon negative electrodes was demonstrated in a fluorine-free electrolyte of 0.5 M NaBPh₄/DME electrolyte. Based on the comparative study of various salts in DME, the NaBPh₄ electrolyte can stabilize the hard carbon/electrolyte interface better than other fluorinated salts, such as NaPF₆, NaFSA, and NaTFSA, suggesting that fluorine components are not indispensable in SEI to stabilize the interface. On the other hand, the selection of solvent is important to fully exert the potential of NaBPh₄. Ether solvents (i.e., DME and THF) enable remarkably better reaction kinetics than carbonate or sulfone, suggesting low interfacial resistance in NaBPh₄/ether electrolytes. The surface analysis of the cycled hard carbon electrodes shows that NaBPh₄ is not subjected to reductive decomposition during cycling and that the SEI is derived from ether solvent. With all things considered, the ether-derived SEI, though containing no fluorine component, is inherently stable and has low resistivity, thus, the combination of ether solvent with reduction-tolerant NaBPh₄ salt is the most effective one to achieve highly reversible and high-rate cycling of hard carbon negative electrodes. This work elucidated the role of salt and solvent in forming a stable SEI on hard carbon, providing a guideline for designing an electrolyte for sodium-ion batteries.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.19-00073.
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