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Short communication

Sodium carboxymethyl cellulose as a potential binder for hard-carbon negative electrodes in sodium-ion batteries

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ABSTRACT

For a non-aqueous sodium-ion battery, a hard-carbon negative electrode with sodium carboxymethyl cellulose (CMC) binder demonstrates the superior reversibility and cycleability in $NaPF_6$ propylene carbonate solution at room temperature to that with ordinary poly(vinylidene difluoride) (PVdF) binder. Furthermore, effects of monofluoroethylene carbonate (FEC) additive remarkably depend on the combination with binders, CMC and PVdF. Surface analyses reveal considerable differences in surface and passivation chemistry which depends on the binders and FEC additive used for the hard-carbon negative electrodes.

1. Introduction

Lithium is an ideal metal element for high energy batteries because of its low redox potential and the second lightest electrochemical equivalent of Li^+/Li next to that of Be^{2+}/Be. Lithium availability does not seem to be particularly limited and expensive compared to transition metals. However, the access to this essential resource could be potentially uncertain when considering large-format application in worldwide in the future. Additionally, the cost of lithium keeps increasing with the prospect of extended application area of Li-ion batteries. Thus, other abundant resources, preferably of low cost, must be investigated as the charge carrier to ensure energy sovereignty, and therefore, Na-ion batteries become the promising device in this regard. As our group has been studying on electrochemical sodium insertion into non-graphitizable carbon (so-called, hard-carbon), the practical and satisfactory performance was first demonstrated for the application to the carbonaceous negative electrode in non-aqueous Na-ion batteries [1]. As generally accepted in lithium-ion chemistry in non-aqueous cells, the use of electrolyte additives is one of the most effective methodologies to improve the battery performance. Recently, FEC additive was found to facilitate the passivation for the electrodes, resulting in better reversibility and cycle life [2].

Recently, hard-carbon is broadly accepted as one of potentially practical negative electrodes for room temperature Na-ion batteries, similar to Li-ion batteries. Its specific reversible capacity in sodium-cells can reach 300 mAh g^{-1} with acceptable capacity retention [3–5]. The hard-carbon can accommodate reversibly sodium atoms, resulting in the formation of $Na_{0.83}C_6$ as formal composition [4]. During the first sodium insertion, passivation layer is formed by the decomposition of the electrolyte, similarly to the lithium insertion [1]. Binders, which are used for the preparation of sheet electrodes from powder materials, have been studied as the essential component to improve the electrochemical/interfacial performance of Li-ion batteries [6]. Furthermore, carboxylate polyanion, polyacrylate, is an efficient binder for improving reversibility of sodiation of a tin electrode [7], however, binders affecting the electrode performance of hard-carbon have not been enough examined.

In this article, we study synergetic effects of binders and electrolyte additive on the electrochemical performance of hard-carbon in sodium cells. Special attention is paid to study the influence of the binders on the reversibility as well as the surface layer and the initial irreversible capacity. Two different binders, CMC and PVdF, are selected and examined for this study. The hard-carbon electrode with CMC demonstrates the excellent reversibility compared to that with ordinary PVdF. Furthermore, the negative and positive effects

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of the FEC additive are observed for the CMC and PVdF electrodes, respectively.

2. Experimental

For electrode preparation commercially available hard-carbon (Carbotron P(J), Kureha Co. [8]) was mixed with PVdF (Polysciences, Inc.) or CMC (Daicel, Ltd.) in the weight ratio 90:10 in N-methypyrrolidon or deionized water, respectively. The resulting slurry was uniformly pasted onto aluminum foil, and then dried at 150 °C for 12 h in a vacuum. The active materials loading was approximately 1.5–3.0 mg cm^{-2} for CMC and PVdF based electrodes. The electrochemical measurements were conducted by using 2032-type coin-cells consisting of the hard-carbon electrode, separator (glass filter, ADVATEC®), electrolyte solution (battery grade, Kishida Chemical Co., Ltd.), and sodium metal (Kanto Chemical, Co., Ltd.) as a counter electrode, and the coin-cells were assembled in a glove box filled with argon. The electrolyte solutions used in this study were basically 1 mol dm^{-3} of $NaPF_6$ propylene carbonate (PC) without or with FEC additive (2% vol.), and 1 mol dm^{-3} $LiClO_4$ or $NaClO_4$ PC. Galvanostatic cycling tests were carried between 0.0 and 2.0 V vs. Na^+/Na at a current density of 25 mA g^{-1}.

After the electrochemical tests, the hard-carbon electrodes was carefully taken out from the coin cells and rinsed with PC and DEC solvent to remove electrolyte, and was dried for 24 h in the glove box. The surface analysis was carried out with scanning electron microscopy (SEM), soft X-ray photoelectron spectroscopy (SOXPES), hard X-ray photoelectron spectroscopy (HAXPES), and time-of-flight secondary ion-mass spectroscopy (TOF-SIMS). X-ray photoelectron spectrometer (JPS-9010MC, JEOL) was used for SOXPES. The spectra were collected at room temperature using a non-monochromatic Mg Kα (1253.6 eV) as incident X-ray source operated at 120 W (12 kV and 10 mA). HAXPES measurement was carried out using a SCIENTA R-4000 at synchrotron facility (BL46XU, SPring-8 in Japan). The excitation energy used for HAXPES was 7939 eV and the total energy resolution was 235 meV. When TOF-SIMS (PHI-TRIFT-V, ULVAC-PHI) was employed for the tested electrode, the targets were bombarded by the 30 keV Au_3^+ beams with a pulsed primary ion current varying.

3. Results and discussion

The effects of PVdF and CMC binders on electrode performance of hard-carbon were examined in the $NaPF_6$ PC solution without or with 2% FEC additive as shown in Fig. 1. The initial capacity of hard-carbon with PVdF was 250 mAh g^{-1} tested in the FEC-free electrolyte, and the capacity was gradually decayed, which is consistent with our previous results tested in the $NaClO_4$ PC solution [2]. Whereas the initial capacity of approximately 250 mAh g^{-1} was similarly observed for all electrodes, the capacity retention depended on the binder and additives. The superior capacity retention above 97% over 100 cycles is achieved for the electrode with CMC in the additive-free electrolyte. The average coulombic efficiency (in 11–100th cycles) and the initial coulombic efficiency, 99.8 and 89.3%, respectively, for the CMC binder are higher than those (99.5 and 86.7%, respectively) for the PVdF binder.

The addition of FEC in electrolyte influences the capacity retention and the coulomb efficiency. Fig. 1b indicates that the FEC addition remarkably improved the cyclability in the case of PVdF as we reported [2]. However, it is noted that the FEC additive has an adverse effect on the CMC electrode as seen in Fig. 1a. Fig. 1c and d show a comparison of the evolution of polarization at the potential close to 0 V tested in the FEC-free solution. Although the polarization and the reversible properties are almost the same during the first cycle for the CMC and PVdF electrodes, the PVdF one suffers from the increase in polarization

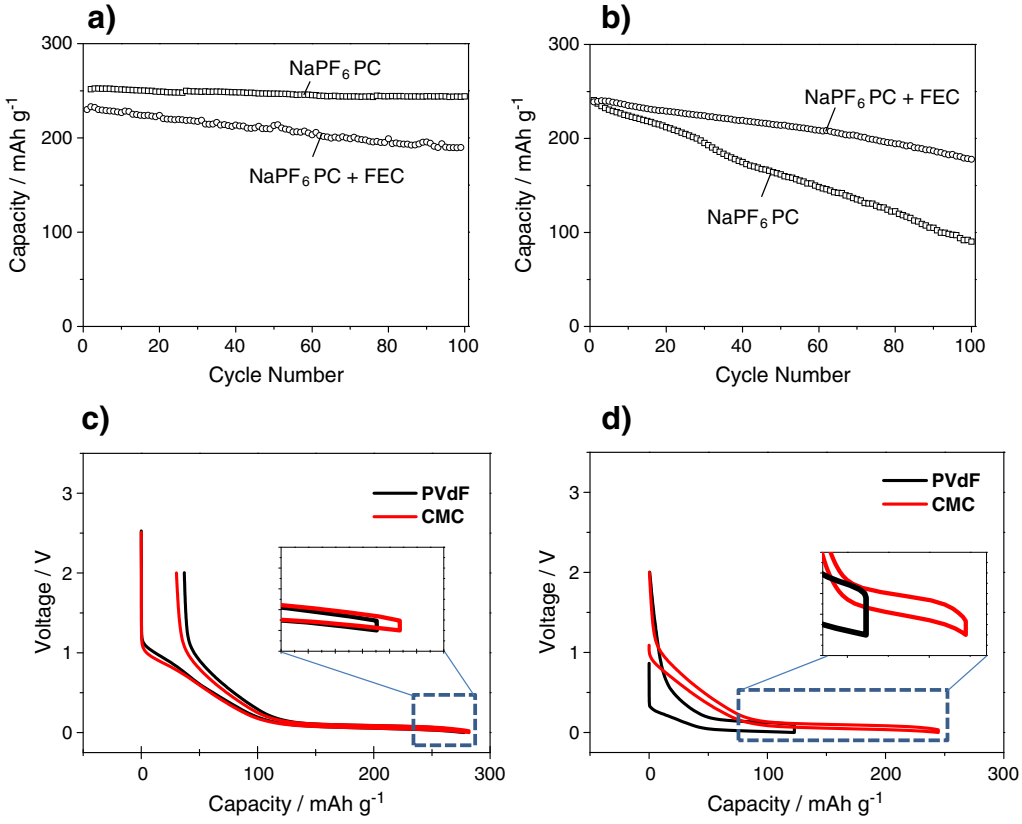

Fig. 1. Cycle performance of hard-carbon electrodes in $NaPF_6$ PC solutions with or without FEC addition: a) CMC and b) PVdF binders. Galvanostatic charge/discharge curves at c) 1st and d) 80th cycles are magnified to compare the difference of polarization.