



## Rubidium and cesium ions as electrolyte additive for improving performance of hard carbon anode in sodium-ion battery



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### ABSTRACT

In this work, rubidium and cesium ions are studied as electrolyte additives for sodium-ion batteries. It is shown that adding small amount of Rb<sup>+</sup> and Cs<sup>+</sup> into the electrolyte significantly modifies the chemical composition of solid electrolyte interphase (SEI) on hard carbon (HC) surfaces, which results in a significant increase in the ionic conductivity and stability of the SEI. The results of this work show that a 0.05 M addition in the form of MPF<sub>6</sub> (M = Rb or Cs) can increase the capacity retention of the Na/HC cells to 95.3% and 97.1% by the Rb<sup>+</sup> and Cs<sup>+</sup> ions, respectively, from 80.6% of the control cell after 100 cycles.

### 1. Introduction

Rubidium and cesium salts have recently been studied as electrolyte additives to improve the cycling efficiency of lithium and graphite anodes in Li-ion batteries. CsPF<sub>6</sub> was first proposed by Zhang et al. to eliminate the formation of Li dendrites in Li-ion batteries via a self-healing electrostatic shield mechanism [1]. Following the description of the electrostatic shield mechanism, it was further found that Cs<sup>+</sup> ions and ethylene carbonate (EC) synergistically promoted the formation of a robust, ultrathin and compact SEI layer on the surface of graphite, which enabled the operation of a graphite anode in a PC-rich electrolyte [2]. In a separate study, Li et al. doped Rb<sup>+</sup> into a layered metal oxide cathode (Li<sub>1.2</sub>Mn<sub>0.54</sub>Co<sub>0.13</sub>Ni<sub>0.13</sub>O<sub>2</sub>). This study found that Rb-doped Li<sub>1.2</sub>Mn<sub>0.54</sub>Co<sub>0.13</sub>Ni<sub>0.13</sub>O<sub>2</sub> increased the (003) interlayer spacing compared to the undoped cathode, resulting in improved rate performance and better cycleability through a decrease in the energy barrier of Li<sup>+</sup> intercalation and deintercalation [3].

Aiming to reduce the cost and meet the demand of large-scale electrochemical energy storage, sodium-ion batteries (SIBs) have been studied due to the abundant resource and low cost of sodium [4]. For the SIBs, HC has been recognized to be a favorable anode material because of its relatively high reversible capacity (~300 mAh g<sup>-1</sup>) and low sodium ion insertion potential [5]. In order to use HC in the SIBs, a suitable electrolyte must be formulated to enable the formation of a robust and protective SEI layer on the surfaces of HC [6]. This SEI layer is required not only to protect the solvents from continuous reduction

but also to provide the path of ionic conduction for stable and fast sodiation-desodiation cycling of Na<sup>+</sup> ions. In the Li-ion community, it is well known that electrolyte additives can effectively improve the formation of an SEI and further stabilize the cycling performance of LIBs [7]. However, few additives are known for SIBs. One additive example is monofluoroethylene carbonate (FEC), which was reported to improve the reversibility of Na-ion batteries [8]. In this work, we explore the utility of Rb<sup>+</sup>, Cs<sup>+</sup> as electrolyte additives for HC anodes in SIBs and discuss the effects Rb<sup>+</sup> and Cs<sup>+</sup> on SEI composition and cell performance.

### 2. Experimental

RbPF<sub>6</sub> and CsPF<sub>6</sub> were synthesized by adding a saturated NH<sub>4</sub>PF<sub>6</sub> aqueous solution into a Rb<sub>2</sub>CO<sub>3</sub> or Cs<sub>2</sub>CO<sub>3</sub> solution, respectively, followed by filtering, recrystallizing and drying [9]. A 0.8 M NaPF<sub>6</sub> solution in a mixed solvent of EC and PC (PC:EC = 4:1, v/v; with 2 wt% FEC) was used as the standard electrolyte. 0.05 M RbPF<sub>6</sub> (or CsPF<sub>6</sub>) was added to the standard electrolyte for the purposes of the study.

Hard carbon (HC, Kureha Extex Co., Ltd.) electrode was calendared with 9 MPa pressure and measured to have approximately 3.5 mg cm<sup>-2</sup> of HC loading. The 2016-type Na/HC coin cells were assembled using a glass fiber membrane as the separator and filled with 250 μL of electrolyte. The cells were cycled on a battery test system (Land CT 2001 A model, Wuhan Jinnuo Electronics Co., Ltd.). Cyclic voltammetry (CV) and AC impedance were measured on a CHI electrochemical

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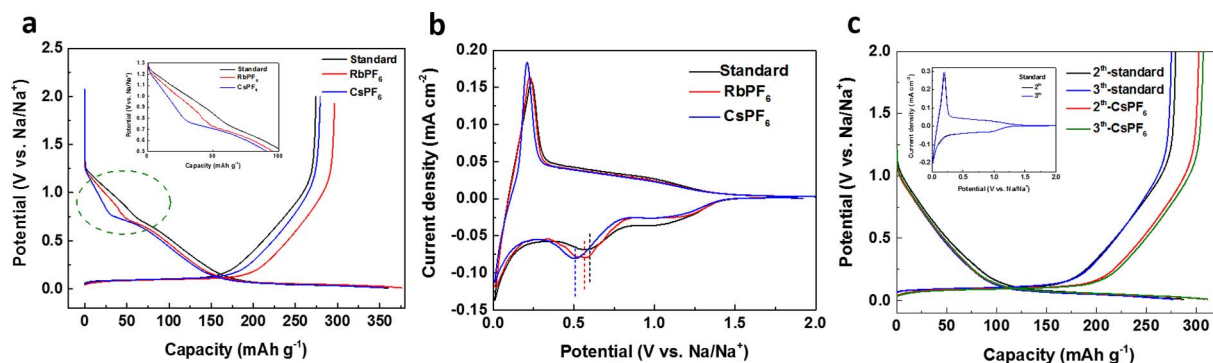


Fig. 1. Electrochemical characteristics of three Na/HC cells with different electrolytes. (a) Voltage profile of the first cycle at 0.05 °C equaling to 15 mA g<sup>-1</sup>, and (b) cyclic voltammogram of the first scanning at 0.05 mV s<sup>-1</sup>, and (c) voltage profiles of the 2nd and 3rd cycle at 0.05 °C.

workstation (CHI 670D, CHI Instrument Co.). The cycled HC electrode was harvested and rinsed using ethyl methyl carbonate in an argon-filled glove-box, followed by analysis using an X-ray photoelectron spectrometer (XPS, Kratos Axis Ultra DLD).

### 3. Results and discussion

Electrochemical characteristics of the initial cycles of Na/HC cells without or with Rb<sup>+</sup> or Cs<sup>+</sup> additive are compared in Fig. 1 by cycling the cell at 0.05 °C (15 mA g<sup>-1</sup>) and scanning at 0.05 mV s<sup>-1</sup>, respectively, between 0.01 V and 2.0 V. Previous publication shows that a PC-EC binary solvent mixture is the best combination for HC anode materials [10]. In LIBs, EC is known to participate in the formation of a robust and effective SEI layer on the graphite anode. A similar effect has also been identified in SIBs; that is, EC solvent is reduced at potentials around 0.8 V vs. Na/Na<sup>+</sup> to form inorganic sodium carbonate, and further reduced at lower potentials to form organic sodium alkylcarbonates with the insoluble reduction products building a protective SEI [11]. The FEC component of the standard electrolyte of this study has been reported to reduce at ~0.7 V vs. Na/Na<sup>+</sup>, which is only slightly higher than the reduction potential of PC [8]. In this work, no significant electrolyte reduction is observed in the potential range from 1.2 V to 0.5 V vs. Na/Na<sup>+</sup> from the standard electrolyte containing 2 wt % FEC. In contrast, a distinct voltage plateau at around 0.75 V is observed from the electrolytes with a 0.05 M RbPF<sub>6</sub> or 0.05 M CsPF<sub>6</sub> added, suggesting significant effect of the Rb<sup>+</sup> and Cs<sup>+</sup> ions on the formation of SEI layer (Fig. 1a).

The effect of Rb<sup>+</sup> and Cs<sup>+</sup> ions is further verified by cyclic voltammetry (CV), as shown in Fig. 1b. It can be seen that the reduction peak current at the potentials between 0.75 V to 0.5 V is increased, and that the reduction potential becomes more negative as a result of the presence of the Rb<sup>+</sup> and Cs<sup>+</sup> ions. It is likely that solvated Rb<sup>+</sup> and Cs<sup>+</sup> ions reduce the LUMO (lowest unoccupied molecular orbital) energy of electrolyte solvents, changing the order of reduction of electrolyte components to form different chemical compositions in the SEI [2]. Regardless of whether or not the cell contains Rb<sup>+</sup> or Cs<sup>+</sup> ions, the charging-discharging voltage profiles and the CV curves become well-overlapped after the 2nd cycle (Fig. 1c), indicating that a protective SEI has been successfully formed in the first cycle of these cells.

XPS characterization is used to understand the effect of Rb<sup>+</sup> (Cs<sup>+</sup>) ions on the chemical composition of SEI layer on the HC surfaces. Generally, the SEI is composed of Na, F, O, C and P elements, as shown in the full spectra (Fig. 2a, measured after the cells were cycled 3 times). The addition of Rb<sup>+</sup> (Cs<sup>+</sup>) ions into electrolyte significantly increases the intensity of Na, F and P peaks, while having little effect on the intensity of O and C peaks. These results reveal that the Rb<sup>+</sup> (Cs<sup>+</sup>) ions are able to promote PF<sub>6</sub><sup>-</sup> anions being decomposed and incorporated into the SEI. The split-fitted F1s spectra (Fig. 2b) shows there are two peaks at around 685.5 eV and 688.6 eV, which can be

assigned to NaF [12] and P–F compounds (possibly Na<sub>x</sub>PF<sub>y</sub>) [13,14] or C–F compounds [15], respectively. Area ratio of the 688.6 eV to 685.5 eV peak is increased to 5.35 for the Rb<sup>+</sup>-added electrolyte and 5.83 for the Cs<sup>+</sup>-added electrolyte, respectively, from 1.89 for the standard electrolyte. Additionally, XPS of the electrodes after 100 cycles is measured and compared with Fig. 2c. It is shown that the F<sub>1s</sub>/O<sub>1s</sub> peak intensity ratio with the addition of Rb<sup>+</sup> and Cs<sup>+</sup> ions changes slightly while that with the standard electrolyte reduces significantly, corresponding to an increase of oxygen content. The above results evidence that the presence of the Rb<sup>+</sup> and Cs<sup>+</sup> ions increases the content of P–F or C–F species in the SEI while suppressing reductive decomposition of the solvents.

Subtle peak intensity of the O 1s spectra and C 1s spectra is also analyzed. As a result of adding Rb<sup>+</sup> or Cs<sup>+</sup> ions, the peak at 537.3 eV (C–O–C(R<sub>1</sub>)) in the standard electrolyte is shifted to 538.2 eV (C–O–C(R<sub>2</sub>)) [16] and the peak area at 535.3 eV (C=O) is shrunk (Fig. 2d). Accordingly, the intensity of the C 1s spectra at 291.8 eV (C–F) and 287.6 eV (C–O) [13] decreases in order from the standard, then Rb<sup>+</sup>-added, and then Cs<sup>+</sup>-added electrolytes (Fig. 2e). The results of Fig. 2d and e indicate that the presence of Rb<sup>+</sup> and Cs<sup>+</sup> ions reduces the relative content of organic moieties in the SEI, as featured by the C=O, C–F, and C–O–C(R<sub>1</sub>) bonds, which can be attributed to the faster diffusion of Rb<sup>+</sup> and Cs<sup>+</sup> ions compared to Na<sup>+</sup> ions in electrochemical processes [17]. Fast diffusion of Rb<sup>+</sup> and Cs<sup>+</sup> is also suggested by the cell reaction resistance discussed below.

The effect of Rb<sup>+</sup> (Cs<sup>+</sup>) ions on the electrochemical performance of Na/HC cells is evaluated by galvanostatic cycling test at 0.1 °C (Fig. 3a and b). Compared with the standard electrolyte cell, the Rb<sup>+</sup> (Cs<sup>+</sup>)-added electrolyte cells show not only higher specific capacity but also more stable capacity retention (Fig. 3a). The capacity and coulombic efficiency of the first cycle at 0.1 °C for three cells with the Rb<sup>+</sup>-added, the Cs<sup>+</sup>-added, and the standard electrolytes, respectively, are in sequence 297 mAh g<sup>-1</sup> (78.9%), 302 mAh g<sup>-1</sup> (78.5%), and 274 mAh g<sup>-1</sup> (76.2%). After the 2nd cycle, all three cells' coulombic efficiency approached 100% and remained constantly (Fig. 3b), whereas the capacity retained 95.3%, 97.1% and 80.6%, respectively, of their initial capacities after 100 cycles. The slightly higher capacity of the cells with Rb<sup>+</sup> or Cs<sup>+</sup> additives can be attributed to the smaller polarization (inset of Fig. 3c), which leads to better utilization of the HC active material. Fig. 3c compares the voltage profiles of these three cells at the 100th cycle. It can be observed that both the Rb<sup>+</sup>-added and Cs<sup>+</sup>-added electrolyte cells suffer much less polarization compared with the standard electrolyte cell. The merit of low polarization in Rb<sup>+</sup> and Cs<sup>+</sup> electrolytes can be explained by the cell impedance results in Fig. 3d. Impedance spectra show the typical suppressed semicircle, followed by a sloped straight line, which was modeled by an equivalent circuit consisting of a bulk resistance (R<sub>b</sub>), a cell reaction resistance (R<sub>ct</sub>), and a Warburg impedance (W) in descending order of frequency [18]. It can be seen that although having the similar R<sub>b</sub>, two cells with

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