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Short communication

A new phenomenon in sodium batteries: Voltage step due to solvent interaction

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ABSTRACT

The galvanostatic cycling of electrode materials in lithium or sodium batteries is assumed to arise just from the contribution of the working electrode, with the counter electrode seen as always operating at a fixed potential. In this manuscript, we demonstrate a hitherto unreported phenomenon which involves a voltage step seen in the discharge profiles at high rates of two-phase electrode materials in sodium batteries that is produced not from a change in potential of the working electrode, but from an increase in polarization of the counter electrode. The choice of solvent used is critical in this context, with the phenomenon existing for EC:PC and not for PC solvent. It arises due to a passivation layer formed on the sodium counter electrode. The voltage step is observed only in the presence of sodium metal as the counter electrode, as it is not seen in full sodium-ion cells.

1. Introduction

In a recent publication, we noticed a voltage step in the galvanostatic profile of $Na_3V_2(PO_4)_3$ during discharge (sodium insertion) when cycled in a sodium half-cell [1]. Interestingly, this voltage step was noticed only at high rates of discharge and was not observed during the charge cycle (sodium extraction). Even more intriguingly, other reports published on this material did not exhibit this voltage step [2–5]. In this manuscript, we report this observed phenomenon on another material, $NaTi_2(PO_4)_3$. This material was chosen due to its flat cycling profile owing to its two-phase sodium storage mechanism, as well as its redox potential ($\approx$2.1 V vs Na/Na^+) lying right in the middle of the electrochemical window of the electrolyte solutions based on alkyl carbonate solvents [6,7]. It will be shown that this voltage step is not caused by any change in the working electrode. Surprisingly, it arises due to an in-situ passivation layer formed on the sodium counter electrode caused by solvent interactions that produce surface species, which form and dissolve during each cycle. The traits of this passivation layer and implications to full sodium-ion cells will be discussed. To the best of our knowledge, this would be the first instance where the galvanostatic cycling profile of a sodium battery is influenced by a passivation layer formed on the counter electrode.

2. Experimental

$NaTi_2(PO_4)_3$ was synthesized using the soft-template approach, the details of which would be reported elsewhere. The electrolytes used were 1 M $NaClO_4$ in ethylene carbonate (EC):propylene carbonate (PC) in a 1:1 volume ratio, and 1 M $NaClO_4$ in PC. For the three-electrode cells, the counter and reference electrodes were a sodium metal disk and ring, respectively. EIS measurements were obtained within 1 MHz–10 mHz. Other relevant information has already been published [8].

3. Results and discussion

Fig. 1a depicts the cycling of $NaTi_2(PO_4)_3$ (NTP) in a two-electrode coin cell versus sodium metal acting as the counter electrode (CE) and reference electrode (RE). The voltage step on discharge in the EC:PC solution at 5C rate is clearly seen. At a low C/5 rate, this step is barely noticeable. The step is also observed at other high rates (e.g., 1, 2 and 10C). This result is analogous to that seen in the discharge profile of $Na_3V_2(PO_4)_3$ (NVP) at high rates [1]. It should be mentioned that the voltage step is witnessed in the EC:PC solution irrespective of the NTP morphology. Surprisingly, when cycled in 1 M $NaClO_4$ in PC, the NTP electrode did not display a voltage step for any C rate (refer to Fig. 1a which displays the cycling profiles at C/5 and 5C as representative examples). Such an observation mirrors the lack of voltage step seen in NVP by other groups, as all other reports published on NVP in the literature use PC as the solvent [2–5]. Since the same material is used as the

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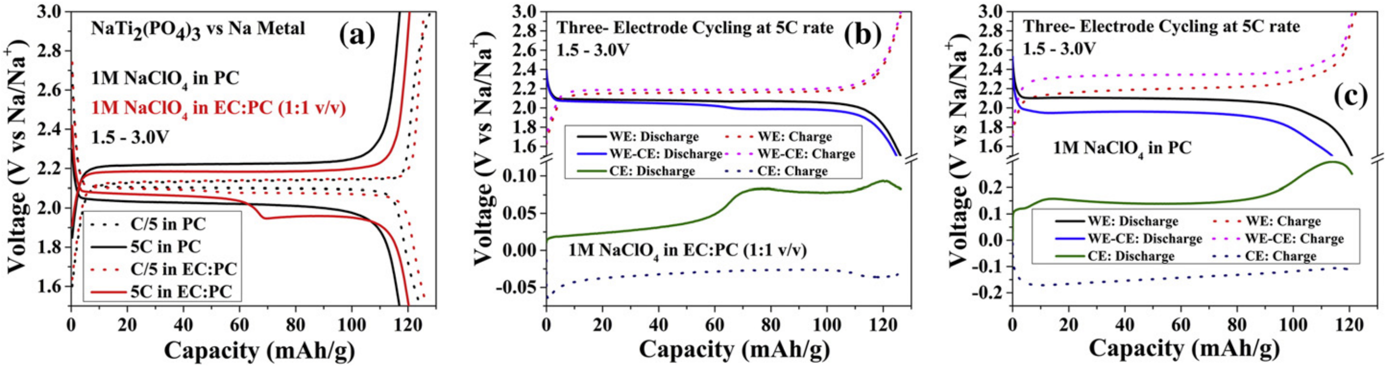

Fig. 1. (a) Illustration of the voltage step phenomenon. Three-electrode cycling for NTP WE against Na CE and RE, in 1 M $NaClO_4$ in EC:PC (b) and PC (c).

working electrode (WE), the voltage step should not arise from the way Na intercalates into the crystal structure of NTP irrespective of the solvents used. This fact is very surprising since the flat plateau nature of the cycling profile, before and after the voltage step, seems to indicate that there could be different two-phase domains or two different energetic sites for inserted Na-ions.

From previous work [9,10], it is well known that WE materials operating within the electrolyte solution's stability zone (away from low voltages which lead to solid-electrolyte interphase formation) may be covered by a passivation layer when they come in contact with the electrolyte solution due to surface interactions of transition metal oxides with electrophilic solvents such as alkyl carbonates. Therefore, it was thought that there could be a passivation layer formed on NTP electrodes which is different in the EC:PC solutions compared to PC, similar to the differences seen on the solid electrolyte interphase (SEI) formed on hard carbon anodes in these solvents [7]. To glean more insight into this unusual voltage step, a three-electrode cell was constructed using EC:PC and PC based solutions. The corresponding cycling curves are presented in Fig. 1b and c, respectively. Surprisingly, the behavior of the WE was found to be identical in both solutions. What was striking was the role of the sodium metal CE upon discharge; in the EC:PC solutions, a clear voltage polarization-step is seen around 65 mAh/g which is absent in pure PC solutions. Hence, it is not a surprise to note that the traditional two-electrodes cycling curve, which is just a result of the cycling profile of the CE subtracted from that of the WE, exhibits the voltage step.

The difference in the polarization of the sodium CE clearly suggests a difference in the way these solutions interact with sodium metal. To understand this interaction, electrochemical impedance spectroscopy (EIS) was performed on three-electrode cells. Firstly, an experiment was undertaken to examine what happens to the sodium CE when a cell is fabricated without any current passing through it. The Nyquist plots of the impedance response of the Na CE as a function of time in both the EC:PC and PC solutions are presented in Fig. 2a and b, respectively. Generally, the Nyquist plots exhibit a semicircle in the high-medium frequency region, and another semicircle in the middle-low frequencies. The high frequency semicircle is attributed to a surface film, the second semicircle at middle-low frequency range arises due to charge transfer and the diameter of each semicircle is a measure of the resistance of the corresponding processes [9]. These features are observed even for lithium electrodes immersed in non-aqueous electrolyte solutions [9,11]. In both solutions, the fresh cell displays a time-varying impedance response, with the general trend being a decrease in the middle-low frequency semicircle and an increase in the high frequency semicircle. This indicates that when Na metal is placed in these solutions, sodium ions are being consumed to form a passivation layer on it. Over time, the passivation layer appears to reach a meta-stable state. Hence, the growth of the passivation layer on the Na CE electrode is time-dependent. Furthermore, the passivation layer formed in the EC:PC solution appears to be more resistive than that formed in the PC solution. It is interesting to note that no significant difference was observed in the Nyquist plots of the NTP electrodes in the EC:PC vs. PC solutions (Fig. 2c). The induction loop seen at low frequencies is believed to be a consequence of the two-phase sodium storage mechanism of NTP [12,13].

To study how these passivation layers change during the course of cycling, EIS plots were obtained at different states of discharge/charge in the EC:PC solutions at 5C rate, as depicted in Fig. 3a. As seen from Fig. 3b, a drastic increase is observed in the resistance of the passivation layer (indicated by the diameter of the high frequency semicircle) formed on the Na CE around the voltage step (points B and C). Upon charge of the cell, the resistance gradually decreases to much smaller values. No significant differences are seen in the corresponding Nyquist plots of the NTP electrode (Fig. 3c). These observations imply two points. Firstly, during the course of cycling, an in-situ surface film of high resistance is formed on the Na CE during discharge which dissolves in the following charging step. This process

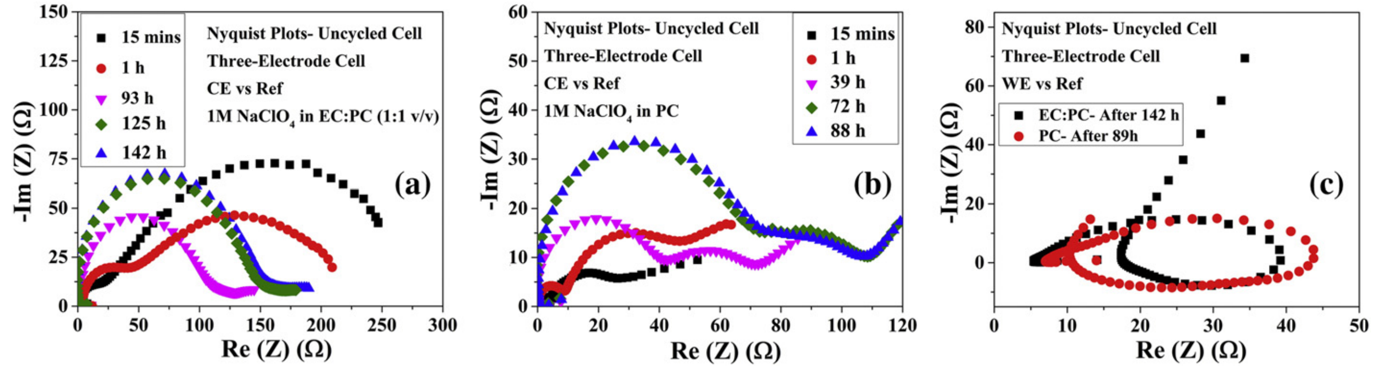

Fig. 2. Nyquist plots for the Na CE as a function of time for uncycled cells in (a) EC:PC and (b) PC solutions. (c) Nyquist plots for the NTP WE in both solutions.