



# Enhanced cycleability and dendrite-free lithium deposition by addition of sodium ion in electrolyte for lithium metal batteries



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## ABSTRACT

The effects of adding sodium (Na) ion into lithium (Li) ion containing organic electrolyte on the cycle behaviors of Li deposition–stripping on  $\text{Li}_{22}\text{Sn}_5$  substrate are investigated. The functions and mechanism of  $\text{Na}^+$  addition to the electrolyte are evaluated through scanning electron microscopy, inductively coupled plasma-atomic emission spectrometry, element mapping, energy dispersive spectrometer, electrochemical impedance spectroscopy, and cyclic voltammetry analyses. The results show that Li–Na co-deposition and co-stripping processes occur during cycles. Utilizing Li–Na co-deposition/stripping reactions to replace the reactions of single Li in organic electrolyte is an effective way to inhibit Li dendrite growth and improve the cycling performance of Li anode in Li metal batteries.

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## 1. Introduction

Using Li metal as the anode for rechargeable batteries is a promising route for achieving high energy density to meet the needs of electronics and automobile applications due to the low redox potential ( $-3.04\text{ V}$  vs. SHE), low density ( $0.59\text{ g cm}^{-3}$ ) and highest specific capacity ( $3860\text{ mAh g}^{-1}$ ) of Li metal among all the solid anode materials [1,2]. However, dendrite formation on Li metal anode remains the most important issue that leads to capacity fading and internal short circuit, which has hindered the practical application of metallic Li rechargeable batteries [3,4].

Researches on Li metal anode have focused on restraining the growth of Li dendrites with diverse countermeasures [5–7]. One of the key factors to cause Li dendrite problem is the inhomogeneous Li deposition on substrates [8]. This could be divided into two stages, i.e., the first layer deposition and the following multilayer deposition. It has been found that the non-uniform deposition in any of these two stages could result in the final Li dendrite formation. Scholars have used Li-containing alloys (e.g., Li–Zn and Li–Sn alloys), instead of pure metallic Li, as anode materials [9,10]. These alloys are only used as substrate for  $\text{Li}^+$  deposition but not for

Li storage. These Li-containing alloy materials can effectively improve the state of first-layer Li deposition. However, the substrate will revert to pure Li as deposition continues. Thus, suppressing dendrite growth is only partially tackled by the new substrate, and new strategy is still needed to make compensation in the following multilayer deposition.

Another approach is the modification of the electrolyte system by optimizing solvents [11],  $\text{Li}^+$  salts [12] and electrolyte additives [13,14] which could improve the multilayer deposition of Li. Addition of small amount of  $\text{Na}^+$  to  $\text{Li}^+$  salt containing ionic liquid electrolyte was reported to be effective to suppress Li dendrite formation [15,16]. But Ref. 16 and Ref. 15 provided different views and results concerning the formation of Li–Na alloy during the deposition–stripping process. Furthermore, the significant improvement was obtained only when the vinylene carbonate (VC) was added into the electrolyte to increase the stability of SEI film. Thus, the improvement in Li deposition/stripping cycling should be considered as a joint contribution of the  $\text{Na}^+$  addition in the electrolyte and the use of electrolyte additive. These results made the question more perplexing.

$\text{Li}^+$  salt is the core of raw materials for electrolytes, which not only provides  $\text{Li}^+$  ions in the electrolyte, but also has important effects on the impedance of the electrolyte, Li metal/electrolyte interface impedance, charge transfer impedance and so on. Excellent  $\text{Li}^+$  salts should have following features: good stability, high

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solubility in organic solvents, easy preparation, non-toxic and environment-friendly. Traditional inorganic  $\text{Li}^+$  salts include lithium perchlorate ( $\text{LiClO}_4$ ), lithium hexafluoroarsenate ( $\text{LiAsF}_6$ ), lithium tetrafluoroborate ( $\text{LiBF}_4$ ), lithium hexafluorophosphate ( $\text{LiPF}_6$ ) and so on. Each of them has its advantages and shortcomings [17–20]. So researchers are still engaged in the study of new  $\text{Li}^+$  salts and organic electrolytes nowadays. Present studies for new  $\text{Li}^+$  salts are focused on the following four categories: sulfonyl lithium salt [ $\text{Li}(\text{CF}_3\text{SO}_3)$  and its derivatives [21], boryl lithium salt [mainly lithium bisoxalato borate ( $\text{LiBOB}$ ), lithium oxalyldifluoroborate ( $\text{LiODFB}$ ), etc.] [22], alkyl lithium salt [ $\text{Li}(\text{C}(\text{SO}_2\text{CF}_3)_3$ ] and imidogen lithium salt [ $\text{Li}(\text{N}(\text{SO}_2\text{CF}_3)_2, \text{LiTFSI}$ ] [23,24]. These new  $\text{Li}^+$  salts are showing potential application prospects due to their high electrochemical stability in electrolytes.  $\text{LiODFB}$  is a novel  $\text{Li}^+$  salt which has drawn much attention since its first report in 2006 [25].  $\text{LiODFB}$  contains the same molecular moieties as those of  $\text{LiBOB}$  and  $\text{LiBF}_4$  [26], the combined advantages of  $\text{LiBOB}$  and  $\text{LiBF}_4$  provide  $\text{LiODFB}$  good SEI film forming characteristics, low temperature performance, high decomposition temperatures (higher than  $240^\circ\text{C}$ ), high decomposition potential (greater than 5.6 V), and good electrochemical performance not only in Li ion batteries [27–30], but also in metallic Li rechargeable batteries [31].

In this work, the effects of  $\text{Na}^+$  ion addition in organic electrolyte on the cycleability was studied with conventional organic solvents and without any other organic additive, i.e.,  $\text{Na}^+$  ion was added in  $1 \text{ mol L}^{-1}$   $\text{LiODFB}$ /ethylene carbonate/dimethyl carbonate (EC: DMC = 1:1 v/v) electrolyte to exclude the influence of ionic liquids. By using electrolyzing method to form  $\text{Na}^+$  in the electrolyte, the  $\text{Li}^+/\text{Na}^+$  dual ion electrolyte with single anion ( $\text{ODFB}^-$ ) was realized, so that the effect of anion could be simplified. In addition, co-deposition/stripping of Na with Li were studied with our newly developed  $\text{Li}_{22}\text{Sn}_5$  substrate [10]. In this way, the effect of  $\text{Na}^+$  on the cycleability of Li deposition/stripping could be protruded based on our previous understanding for the effects of  $\text{LiODFB}$  salt and  $\text{Li}_{22}\text{Sn}_5$  substrate on the performance of Li metal anode. Furthermore,  $\text{Na}^+$  concentration was increased to  $0.125 \text{ mol L}^{-1}$  to ensure the co-deposition/co-stripping processes of both Li and Na elements in the cycling tests. The cycleability of the Li anode was evaluated and the improvement mechanism was analyzed under such conditions.

## 2. Experimental

### 2.1. Preparation of $\text{Li}_{22}\text{Sn}_5$ substrate electrode

$\text{Li}_{22}\text{Sn}_5$  alloy was used as the substrate of the Li electrode because of its unique features in improving the smooth morphology of Li deposit in the initial stage of Li deposition. The alloy was prepared through the previously reported procedure [10]. Briefly, a Cu electrode was made with a rounded copper (Cu) rod wrapped in a polytetrafluoroethylene (PTFE) rod. The surface of the Cu electrode was mirror polished and cleaned with ultrapure water. Then, the Sn precursor layer was prepared through electrodeposition on the Cu electrode from a  $\text{Sn}^{2+}$  containing aqueous solution. Finally,  $\text{Li}^+$  was deposited on the Sn substrate precursor to form the  $\text{Li}_{22}\text{Sn}_5$  alloy in  $1 \text{ mol L}^{-1}$   $\text{LiODFB}$ /EC+DMC (1:1 v/v) electrolyte solution, of which the salt  $\text{LiODFB}$  was purchased from Sigma-Aldrich (purity 99%), and the electrolyte solution was prepared in our laboratory; the Li deposition was performed in an Argon gas-filled glove box (Etelux 2000, China).

### 2.2. Morphology observation and composition analysis

The surface morphologies of the  $\text{Li}_{22}\text{Sn}_5$  substrate and Li deposits on the substrate under different conditions were observed

using SEM (Merlin Compact, Carl Zeiss AG). The surface elemental components of Li deposits in the  $\text{Na}^+$  containing electrolyte were analyzed by EDS (INCA, Oxford Instruments). The elemental composition of the deposited films was determined by ICP–AES (CAP 7000, Thermo Fisher Scientific).

### 2.3. Electrochemical measurements

The galvanostatic charge–discharge cycling experiments for Li deposition–stripping were conducted using Land CT2001A Battery Tester (LANHE, China), performed in a three-electrode cell using  $\text{Li}_{22}\text{Sn}_5$  substrate as the working electrode, Li foil as the counter and reference electrodes. CV was performed with CHI 611b electrochemical workstation (Chenhua, China) at a scan rate of  $0.1 \text{ mV s}^{-1}$  in a three-electrode cell, with glassy carbon as working electrode and Li foil as counter and reference electrodes. The electrode/electrolyte interface impedance was analyzed with electrochemical impedance spectrum (EIS) conducted with Reference 600 Potentiostat (GAMRY Instruments, USA) in frequency range of  $10^5 \text{ Hz}$  to  $10^{-2} \text{ Hz}$ , performed in a three-electrode cell using  $\text{Li}_{22}\text{Sn}_5$  substrate as the working electrode, Li foil as the counter and reference electrodes. The electrolytes of  $1 \text{ mol L}^{-1}$   $\text{LiODFB}$ /EC+DMC (1:1 v/v) and  $1 \text{ mol L}^{-1}$   $\text{LiODFB}$  +  $0.13 \text{ mol L}^{-1}$   $\text{NaODFB}$ /EC+DMC (1:1 v/v) were used for the tests.

## 3. Results and discussion

For the study of the effects of  $\text{Na}^+$  addition in electrolyte on the performance of Li deposition/stripping, the impact of the anion in the  $\text{Na}^+$  salt should be avoided, in other words, the  $\text{Na}^+$  salt should have the same anion with  $\text{Li}^+$  salt in the electrolyte. Due to this reason, the preparation of  $\text{Na}^+$  additive was realized using electrolytic method in the  $\text{Li}^+$  salt containing electrolyte. Na metal and Li metal were chosen as anode and cathode, respectively. The electrolyte was  $1 \text{ mol L}^{-1}$   $\text{LiODFB}$ /EC+DMC (1:1 v/v), then a continuous electrolysis was carried out quantitatively, and  $\text{Li}^+$  was partly replaced by  $\text{Na}^+$  to form mixed electrolyte solution– $x\text{LiODFB}+y\text{NaODFB}$ /EC+DMC (1:1 v/v). After this, certain amount of  $\text{LiODFB}$  was added into the electrolyte solution to compensate the consumption of  $\text{Li}^+$ . ICP–AES testing was used to prove the validity of this electrolytic method. Sample 1 represents the electrolyte after electrolyzed for 60 min at current density of  $10 \text{ mA cm}^{-2}$ , and the volume of the electrolyte was 3 ml; sample 2 represents the electrolyte after electrolyzed for 30 min at current density of  $10 \text{ mA cm}^{-2}$ , and the volume of the electrolyte was 2.5 ml. The test results are shown in Table 1. Meanwhile, the theoretical concentrations were calculated via Faraday's law of electrolysis. The results demonstrated that  $\text{Na}^+$  ions exist in electrolyte solution indeed and its concentration was very close to the theoretical calculation value. According to this method, a set of dual cation electrolyte solutions with  $\text{Na}^+$  concentrations of  $0.50 \text{ mol L}^{-1}$ ,  $0.25 \text{ mol L}^{-1}$ ,  $0.13 \text{ mol L}^{-1}$ ,  $0.06 \text{ mol L}^{-1}$ ,  $0.03 \text{ mol L}^{-1}$  respectively, were prepared.

The Li deposition–stripping cycle performance on the  $\text{Li}_{22}\text{Sn}_5$  substrate was tested in both  $\text{Li}^+$  containing and  $\text{Li}^+ + \text{Na}^+$  containing electrolytes. The cycling conditions were set in a constant Coulombic efficiency ( $E_c$ ) and an upper potential limit of 3.0 V.  $E_c$  can be expressed as a ratio of  $Q_s/Q_d$ , where the  $Q_d$  and  $Q_s$  represent the electrical charge of Li deposition and stripping in each cycle respectively. The  $E_c$  value in each cycle can be calculated by the following equation:

$$E_c = \frac{Q_s}{Q_d} \times 100\% \quad (1)$$

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