Enhanced cycleability and dendrite-free lithium deposition by adding potassium ion to the electrolyte for lithium metal batteries

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ABSTRACT

The effects of adding potassium ion (K^+) to lithium oxalyldifluroborate (LiODFB)/ethylene carbonate (EC) + dimethyl carbonate (DMC) (1:1 vol.%) electrolyte on the cycle behaviors of lithium deposition–stripping on a $Li_{22}Sn_5$ substrate electrode are investigated. The functions and mechanism of K^+ addition to the electrolyte are evaluated through scanning electron microscopy (SEM), inductively coupled plasma-atomic emission spectrometry (ICP–AES), element mapping, energy dispersive spectrometer (EDS), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV) analyses. The addition of K^+ to the electrolyte significantly improves the morphology of the lithium deposits and the cycleability of lithium deposition–stripping. K^+ is not reduced nor incorporated on the substrate during lithium deposition. Based on the reported "self-healing electrostatic shield" (SHES) mechanism, this study proposes the SHES–kinetics mechanism, which considers both kinetic and thermodynamic factors.

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1. Introduction

Lithium (Li) metal has long been considered as the ideal anode material for next-generation energy storage systems because of its highest theoretical specific capacity ($3860\,mAh\,g^{-1}$) among the solid materials, low redox potential ($-3.040\,V$, vs. SHE), and low density ($0.59\,g\,cm^{-3}$) [1,2]. Although extensive attempts have been made to use Li as anode in rechargeable batteries since the 1970s [3], this metal anode has not been commercialized for large-scale applications [4]. The two main issues that should be addressed prior to commercialization of Li anode include growth of Li dendrites and limited coulombic efficiency during Li deposition–stripping cycles [5]. Growth of Li dendrites can lead to internal short circuit, resulting in fire or other safety problems [6].

Li-ion batteries, which utilize graphite as anode, have been successfully commercialized for portable electronic devices since the 1990s. However, the energy density of graphite-based Li-ion batteries is predicted to reach their limit in the near future after more than 20 years' development [3]. In this regard, Li metal anode material has attracted considerable attention [7–13], particularly with the emergence of Li–S [14,15] and Li–O_2 [16–18] batteries, for its theoretical capacity is 10 times higher than that of graphite.

Research on the use of Li metal as anode has focused on restraining the growth of Li dendrites [19–22]. Scholars have used Li-containing alloys (e.g., lithium–zinc and lithium–stannum alloys), instead of pure metallic Li, as anode materials [23,24]. These alloys are only used as substrates for Li^+ deposition but not for Li storage. $Li_{22}Sn_5$ material is an example of such alloys which can effectively improve the state of Li^+ first-layer deposition. However, the substrate will revert to pure Li as deposition continues. Thus, suppressing dendrite growth has not been effectively resolved yet. Another approach is modification of the electrolyte system by optimizing solvents [25], salts [26], and electrolyte additives [27]. Ding et al. [28] proposed a novel mechanism called "self-healing electrostatic shield (SHES)," which can fundamentally alter dendrite formation in electrochemically deposited Li films. Low concentrations of selected cations [cesium ion (Cs^+) or rubidium ion (Ru^+)] exhibit effective reduction potentials below the standard reduction potential of Li^+. During Li^+ deposition, these additive cations form a positively charged electrostatic shield around the initial grown tips of the protuberances of Li deposits without reduction and deposition. This process induces deposition of Li^+ to the adjacent regions of the protuberances and eliminates dendrite formation. This feature can be considered as thermodynamic factors that restrict the behavior of Li deposition.

Potassium, cesium and rubidium, which belong to the same group in the periodic table of elements, exhibit similar chemical

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properties. According to the Nernst equation [Eq. (1)], when the K$^+$ concentration is decreased to 0.001 mol L^{-1}, the reduction potential of K$^+$ shifts to −3.108 V (vs. SHE), which is lower than the standard reduction potential of Li$^+$ (−3.040 V, vs. SHE). K$^+$ is assumed to have a similar effect to that of Cs$^+$ and Rb$^+$. Thus, in the present study, K$^+$ was selected as candidate additive to the electrolyte. Basing on the experimental results, we propose a modified SHES mechanism called the "self-healing electrostatic shield–kinetics mechanism," which comprehensively considers both kinetic and thermodynamic factors.

On the other side, the lithium salt, which is the core of raw materials for electrolytes, is the provider of Li ions in the electrolyte, and has important effect on the impedance of the electrolyte, lithium metal surface impedance, charge transfer impedance and so on. Excellent lithium salts should have following features: good stability, soluble in organic solvents, easy preparation, non-toxic and environment-friendly. Traditional inorganic lithium salts including lithium perchlorate (LiClO$_4$), lithium hexafluoroarsenate (LiAsF$_6$), lithium tetrafluoroborate (LiBF$_4$), lithium hexafluorophosphate (LiPF$_6$) and so on. They each have their advantages, but also shortcomings [29–32]. So researchers turned to the study of new organic electrolytes nowadays. The present study is focused on the following four categories: sulfonyl lithium salt [Li(CF$_3$SO$_3$) and its derivatives [33], boryl lithium salt [mainly lithium bisoxalatoborate (LiBOB), lithium oxalyldifluroborate (LiODFB), etc.] [34], alkyl lithium salt [LiC(SO$_2$CF$_3$)$_3$] and imidogen lithium salt [LiN(SO$_2$CF$_3$)$_2$, LiTFSI] [35,36]. These new lithium salts are showing potential application prospect due to their high electrochemical stability in electrolytes. LiODFB is a novel lithium salt which has been drawn much attention since it was first reported in 2006 [37]. LiODFB containing the same molecular moieties as those of LiBOB and LiBF$_4$ [38], has the combined advantages of LiBOB and LiBF$_4$. It has good SEI film forming characteristics, low temperature performance, high decomposition temperatures (higher than 240 °C) and high decomposition potential (greater than 5.6 V), showing good electrochemical performances in lithium-ion batteries [39–42]. But there are few reports about the use of LiODFB in metallic lithium rechargeable batteries. Therefore in this work we choose LiODFB but not LiPF$_6$ as the lithium salt for the electrolyte.

2. Experimental

2.1. Preparation of Li$_{22}$Sn$_5$ substrate

In this work, the Li$_{22}$Sn$_5$ alloy was selected as substrate of the Li electrode because of its unique characteristics in improving Li smooth deposition. The alloy was prepared through a previously reported procedure [24]. Li$^+$ was initially deposited on the Sn substrate precursor to form the Li$_{22}$Sn$_5$ alloy in the electrolyte, namely, 1 mol L^{-1} LiODFB/ethylene carbonate (EC) + dimethyl carbonate (DMC) (1:1 vol.%) solution; the deposition was performed in a specially designed electrolytic cell, which was assembled in an Argon gas-filled glove box (Etelux 2000, China). The Sn precursor was fabricated through electrodeposition of Sn on the Cu electrode from an aqueous solution. The electrode was a rounded Cu rod wrapped in a polytetrafluoroethylene (PTFE) rod. The surface of the Cu electrode was polished smoothly and cleaned with ultrapure water before the electrodeposition of Sn.

2.2. Morphology and composition determination

The surface morphologies of the Li$_{22}$Sn$_5$ substrate and Li deposits on the substrate under different conditions were determined using SEM (Merlin Compact, Carl Zeiss AG). The surface elemental components of Li deposits in the K$^+$ 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). The polarization characteristics of Li$^+$ deposition on the substrates were evaluated by linear sweep voltammetry (LSV) with CHI 611b Electrochemical Workstation (Chenhua, China). CV was performed with CHI 611b Electrochemical Workstation at a scan rate of 0.1 mV s^{-1} in a three-electrode cell, with glassy carbon as working electrode and Li foil as counter and reference electrodes. EIS was conducted with Reference 600 Potentiostat (GAMRY Instruments, USA) at a frequency range of 10^5 Hz to 10^{-2} Hz. The electrolytes of 1 mol L^{-1} LiODFB/EC + DMC (1:1 vol.%) solution with different concentrations of KClO$_4$ were used for the tests.

3. Results and Discussion

According to the Nernst equation,

$$E_{Red} = E_{Red}^0 - \frac{RT}{zF} ln \frac{a_{Red}}{a_{Ox}} \qquad (1)$$

where R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (298.15 K), and a is the activity of the relevant species (a_{Red} and a_{Ox} are for the reductant and oxidant, respectively), z is the number of moles of transferred electrons, and F is the Faraday constant (9.6485 × 10^4 C mol^{-1}). In the case of low concentration, a can be replaced by concentration c. At room temperature, Eq. (1) can be simplified as:

$$E_{Red} = E_{Red}^0 - \frac{0.05916V}{z} lg \frac{1}{c_{Ox}} \qquad (2)$$

The maximum concentration of K$^+$ that exhibits an effective reduction potential below the standard potential of Li/Li$^+$ is 0.0144 mol L^{-1}, which is calculated using Eq. (2). The saturated concentration of KClO$_4$ in 1 mol L^{-1} LiODFB/EC + DMC (1:1 vol. %) is 0.01044 mol L^{-1}, as determined using ICP–AES method. Thus, 0.01, 0.005, and 0.001 mol L^{-1} K$^+$ were selected to evaluate the effects of K$^+$ addition to the electrolyte. The effective reduction potential of K$^+$ at various concentrations is calculated according to Eq. (2), and the results are listed in Table 1. The standard electrode potential of K/K$^+$ is −2.931 V, which is higher than that of Li/Li$^+$ (−3.040 V). However, when the K$^+$ concentration is decreased to a certain degree, such as 0.01 and 0.001 mol L^{-1}, the effective reduction potential of K/K$^+$ shifts to −3.049 and −3.108 V, respectively. This condition satisfies the prerequisite for the occurrence of the SHES mechanism.

A series of electrochemical tests were conducted to verify the effectiveness of adding K$^+$ to the electrolyte to improve Li deposition–stripping cycling characteristics. First, the deposition-–stripping cycle performance of Li on the Li$_{22}$Sn$_5$ substrate in different electrolytes were tested and compared, the results are shown in Fig. 1. The electrolyte, namely, 1 mol L^{-1} LiODFB/EC + DMC

Table 1
Effective reduction potential of Li$^+$ and K$^+$ at different concentrations.

Cation	E^0 (V)	Effective reduction potential (V, vs. SHE)		
	1 mol L^{-1}	0.01 mol L^{-1}	0.005 mol L^{-1}	0.001 mol L^{-1}
Li$^+$	−3.040	/	/	/
K$^+$	−2.931	−3.049	−3.067	−3.108