Lithium metal batteries (LMBs) are considered as the development direction of next-generation rechargeable lithium batteries owing to their high energy densities. The electrochemical and safety performances of LMBs are significantly influenced by the solid electrolyte interphase (SEI) formed on the surface of lithium anode. Herein, the effects of both salt concentration and temperature on the SEI composition and properties are systematically investigated. The results reveal that either reducing the salt concentration to ultralow levels or elevating the temperature can lead to a more complete decomposition of the LiFSI salt. Meanwhile, the LiNO₃-rich SEI formed in the most dilute electrolyte (0.1 M) exhibits a better protective effect on lithium metal than the Li₄N-rich SEI formed in other electrolytes with higher salt concentrations. Benefiting from the compact and stable SEI, Li₄Li₃Ti₃O₁₂ batteries using the 0.1 M electrolyte possess the most superior cycling and rate performance at high temperature. This work generates a holistic understanding of the synergistic effects of salt concentration and temperature on SEI. Moreover, the utilization of dilute electrolytes not only renders a superior electrochemical performance of batteries at high temperature, but can also lower the production cost of electrolytes, showing a promising application potential in LMBs.

1. Introduction

Lithium metal batteries (LMBs) have been regarded as the most promising candidate for the next-generation high energy density batteries. However, the practical application of LMBs has long been hindered by their inferior cycle stabilities and safety hazards. In LMBs, the solid electrolyte interphase (SEI) is a passivating layer formed between the lithium anode and the electrolyte, whose chemical composition and properties can often determine the electrochemical and safety performance of batteries. Therefore, factors that can affect the properties of the SEI layer have attracted considerable attention and been extensively studied.

Many factors have been confirmed to have pronounced influences on the SEI compositions and properties, such as anode materials, electrolyte formulations, salt concentrations, electrochemical conditions, and temperature. Among them, the salt concentration is often overlooked because an intermediate level of salt concentration (e.g., 1 M) is generally adopted, which can bring about the most superior ionic conductivities for the electrolytes and thus the best battery performances. However, Suo et al. proposed a new class of “solvent-in-salt” (SIS) electrolyte with ultrahigh salt concentrations and found that the thickness of the formed SEI declined with increasing salt concentration, contributing to better lithium cycling efficiencies. Shi et al. reported a highly concentrated phosphate-based electrolyte that could generate a stable LiF-rich SEI layer on the lithium electrode. The LiF-rich SEI could suppress the lithium dendrite growth and considerably enhanced the cycle stability and safety of lithium batteries. Thus, it is of significant importance to...
explore the correlation between salt concentration and SEI properties for LMBs.\textsuperscript{[39–45]} Meanwhile, the chemical composition and properties of SEI are temperature sensitive.\textsuperscript{[46]} The unstable organic species in SEI tend to decompose into more stable inorganic components at high temperature, which can greatly alter the mechanical property and ionic conductivity of the SEI.\textsuperscript{[47]} In addition, the SEI is prone to grow persistently at elevated temperature, which causes continuous loss of the electrolyte and active lithium and increases the cell impedance, resulting in fast fading of capacity and power density of the cells.\textsuperscript{[32,48,49]} Although the influence of salt concentration and temperature on the SEI properties and battery performance have been substantially studied in a separate way, comprehensive research taking both of these two factors into account is rare to date.

In this work, we investigated the synergistic effects of salt concentration and temperature on the chemical composition and properties of SEI. It is found that the LiFSI salt can decompose more completely by either reducing the salt concentration to an ultralow level or elevating the temperature. The complete degradation of LiFSI salt in the most dilute electrolyte (0.1 M) tends to produce LiNO\textsubscript{3}-rich SEI, while Li\textsubscript{3}N-rich SEI is more likely to form in the electrolytes with higher salt concentrations. At high temperature, the LiNO\textsubscript{3}-rich SEI exhibits a better protective effect on metallic lithium than the Li\textsubscript{3}N-rich SEI, inhibiting lithium metal corrosion and continuous electrolyte consumption. The superior SEI renders Li|Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} batteries using the 0.1 M electrolyte the most outstanding cyclic and rate performance at high temperature.

2. Results and Discussion

Preliminary experiments were conducted to explore the influence of solvent formulations on the electrochemical performance of batteries. Three solvent systems, namely, ethylene carbonate (EC), ethylene carbonate/dimethyl carbonate (EC:DMC, 1:1 in volume), and ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC:DMC:DEC, 1:1:1 in volume), all of which dissolved 5 M LiFSI salt, were used as electrolytes. The electrochemical cycling tests reveal that the LiCu battery using the ternary solvents electrolyte possesses the highest cycle stability (Figure S1, Supporting Information), indicating side reactions are less likely to occur in the ternary solvents electrolyte compared with the other two solvent formulations during cycling. Thereby, the ternary solvents system of EC/DMC/DEC (1:1:1 in volume) were adopted for subsequent experiments to probe the effects of salt concentration and temperature on the SEI properties.

The protective effect of the SEI constructed in electrolytes with different salt concentrations on metallic lithium was evaluated in Li|Cu cells at room temperature and 90 °C, with a lithium deposition areal capacity of 0.5 mAh cm\textsuperscript{-2} at the current density of 0.5 mA cm\textsuperscript{-2}. Postmortem analysis was conducted on the copper electrodes after lithium plating. From the scanning electron microscope (SEM) and optical images in Figure 1a–d, it is clear that copper electrodes in all electrolytes are uniformly covered by deposited lithium at room temperature, but differences in the deposition morphology could be identified from corresponding SEM images. The lithium metal in the 0.1 and 1 M electrolytes tends to form granular deposits, while in the electrolytes with

![Figure 1](image-url)

**Figure 1.** The deposition morphologies of lithium metal in electrolytes with different salt concentrations: a) 0.1 M, b) 1 M, c) 5 M, and d) 10 M at room temperature and e,i) 0.1 M, f,j) 1 M, g,k) 5 M, and h,l) 10 M at 90 °C. The insets display optical images of the corresponding copper electrodes after lithium plating.
higher salt concentrations (5 and 10 M), it is more prone to form porous mosslike structures. However, significant difference in the deposition behavior of lithium metal was found at the elevated temperature of 90 °C. The optical images (Figure 1e–h inset) reveal that only the copper electrode in the 0.1 M electrolyte has a uniform and compact deposition layer, while in the other electrolytes, the corrosion of the deposited lithium metal is fairly obvious. This indicates that, at high temperature, the SEI layer formed in the most dilute electrolyte (0.1 M) is more stable than that in electrolytes with higher salt concentrations. The stable SEI can effectively prevent lithium metal from continuously reacting with the electrolytes, reducing metallic lithium corrosion and electrolyte consumption. Moreover, it is noteworthy that the deposited Li metal in the high salt concentration electrolytes (5 and 10 M) possesses rougher and porous surface structures (Figure 1k,h and S2, Supporting Information). These porous structures can significantly enlarge the interface area and may exacerbate the side reactions between electrolyte and electrodes, which can bring adverse effects on the cyclic and safety performance of batteries at high temperature.

X-ray photoelectron spectroscopy (XPS) was conducted to gain information on the chemical composition of the SEI formed in electrolytes with various salt concentrations at room temperature and 90 °C. As shown in Figure 2, the SEI layer formed in all electrolytes contain N and F elements, indicating the LiFSI salt has participated in the construction of SEI to varying extents. Four peaks at 407.2, 403.2, 399.8, and 398.4 eV in the N 1s spectra can be ascribed to LiNO3, N—O, NSO2–, and LiN, respectively (Figure 2a,e,i,m). At room temperature, NSO2– is the only nitride species discernible, exhibiting the most complete decomposition of the LiFSI electrolyte. This component is supposed to stem from direct cleavage of the S–F bond in LiFSI, suggesting an incomplete decomposition of the lithium salt. In electrolytes with higher salt concentrations (5 and 10 M), a portion of the NSO2– species in SEI has further decomposed into LiNO3. In contrast, the LiNO3 becomes the dominant nitrogen-containing compound in SEI formed in the most dilute electrolyte (0.1 M), with no peaks for the NSO2– species discernible, indicating the most complete decomposition of the LiFSI. Salt degradation can also be observed in the F 1s spectra (Figure 2b,f,j,n). Another species derived from the incomplete decomposition of LiFSI salt, −SO2F (687.8 eV), can be detected in SEI of almost all electrolytes except the 0.1 M electrolyte, indicating that the most complete decomposition of the LiFSI salt occurs in the most dilute electrolyte again. At 90 °C, the chemical composition of the SEI formed in the 0.1 M electrolyte remains unchanged in comparison with that at room temperature, reflecting the stability of the LiNO3 and LiF components. By contrast, the commonly existing SEI component in the 1, 5, and 10 M electrolytes at room temperature, NSO2–, has decomposed into more stable LiNO3 and LiN at elevated temperature. A notable trend is more LiN but less LiNO3 appears in SEI as the salt concentration increases (Figure 2d,h,l,p). This trend, accompanied with the lithium deposition morphologies (Figure 1e–h), suggests that although LiN is considered as a desired SEI component because of its high lithium-ion conductivity,53 its protective effect on metallic lithium is not as good as LiNO3 at high temperature. Moreover, the peaks in the S 2p spectra can be fitted into three doublets (Figure 2c,g,k,o). The S 2p1/2 peaks at 169.9, 168.6, and 166.5 eV can be ascribed to NSO2–, Li2S2O4, and Li2SO4, respectively.52–55 There are no characteristic peaks in the S 2p spectra of the 0.1 M electrolyte, which indicates few LiFSI has taken part in the formation of SEI. Meanwhile, Li2SO4 can only be observed in the 10 M electrolyte, suggesting that complete decomposition of LiFSI can also be achieved at ultrahigh salt concentrations.

To understand the influence of SEI on the electrochemical performance of batteries, the cycling and rate performances of Li|Li14Ti2O12 batteries using electrolytes with different salt concentrations were investigated at room temperature and 90 °C. When operating at room temperature, all batteries exhibit comparable cycle stabilities, with coulombic efficiencies reaching nearly 100% after the first few cycles (Figure S3, Supporting Information). At elevated temperature of 90 °C, the cyclic stabilities of Li|Li14Ti2O12 batteries with different electrolytes show varying degrees of reduction, which can be ascribed to the intensified side reactions at high temperature. But surprisingly, the most dilute electrolyte (0.1 M) now possesses the best cycle stability, delivering a decent specific capacity of 144.2 mAh g−1 after 150 cycles (Figure 3a). In contrast, the Li|Li14Ti2O12 batteries utilizing the 1, 5, and 10 M electrolytes experience serious capacity decay after 40, 20, and 5 cycles, respectively. Furthermore, the first-cycle coulombic efficiency declines with increasing salt concentrations, exhibiting 94.9%, 87.2%, 62.7%, and 44.5% for the 0.1, 1, 5, and 10 M electrolytes, respectively (Figure 3b). The most superior cycle stability and highest first-cycle coulombic efficiency of the 0.1 M electrolyte can be reasonably attributed to the stable SEI formed in this electrolyte, which has the best protective effect on metallic lithium and impedes continuous consumption of the electrolyte and active lithium. The rate capability of batteries using electrolytes with different salt concentrations was tested at room temperature and 90 °C. As shown in Figure 3c, batteries using the 1 and 5 M electrolytes hold acceptable rate capability at room temperature, with capacity retentions of 65% and 62% at 5 °C, respectively. In contrast, batteries with 0.1 and 10 M electrolytes can merely provide specific capacities of 25.5 and 23.9 mAh g−1, respectively, at 5 °C, only maintaining 15% and 14% of their capacities at 0.1 °C. The inferior rate capability of the 0.1 and 10 M electrolytes can be mainly attributed to their inadequate ionic conductivities at room temperature, as evidenced in Figure S4, Supporting Information. However, the correlation between the salt concentration and the rate performance of electrolytes has changed considerably at 90 °C (Figure 3d). The core difference is that the battery using the most dilute electrolyte (0.1 M) now exhibits the most superior rate capability among all batteries. This change can be partly ascribed to the “compensation effect” of temperature, which increases the ionic conductivity of the 0.1 M electrolyte to some extent. But more importantly, side reactions taking place at the interfaces between electrolyte and electrodes get aggravated at high temperature, rendering the stability of SEI decisive for the battery performance. Therefore, the stable LiNO3-rich SEI formed in the 0.1 M electrolyte brings about the most superior cyclic and rate performance of Li|Li14Ti2O12 batteries at high temperature.

Based on the aforementioned results and discussions, the synergistic effects of salt concentration and temperature on the chemical composition and properties of SEI are shown in Figure 4. At room temperature, the NSO2– component commonly exists in SEI except the one formed in the most dilute...
Figure 2. XPS results of N 1s, F 1s, and S 2p spectra for the SEI formed on the surface of deposited lithium metal in electrolytes with various concentrations: a–c) 0.1 M, e–g) 1 M, i–k) 5 M, and m–o) 10 M at room temperature and 90 °C. Relative contents of different chemical compositions from the XPS spectra are given in d), h), l), and p), respectively.
electrolyte (0.1 M), suggesting a more complete salt degradation occurs when reducing the salt concentration to ultralow levels. At elevated temperature of 90 °C, the NSO$_2^-$ species will further decompose into more stable LiNO$_3$ and Li$_3$N components. Therefore, either reducing the salt concentration or elevating the temperature can render a more complete decomposition of lithium salt. However, unlike the other electrolytes with higher salt concentrations where Li$_3$N is favored in SEI at high temperature, LiNO$_3$ dominates the nitrogen compounds of the SEI formed in the 0.1 M electrolyte. The LiNO$_3$-rich SEI in the most dilute electrolyte is evidenced to have the best protective effect on metallic lithium at high temperature, leading to the most superior high-temperature cycling and rate performance of Li|Li$_4$Ti$_5$O$_{12}$ batteries.

3. Conclusion

In summary, the effects of both salt concentration and temperature on the chemical composition and properties of the SEI formed on lithium metal have been systematically investigated. It is found that the LiFSI salt exhibits a complete decomposition in the most dilute electrolyte (0.1 M) both at room temperature and 90 °C. In contrast, the incomplete decomposition products, such as NSO$_2^-$ and $-$SO$_2$F, commonly exist in the SEI of other electrolytes at room temperature. However, at 90 °C, these species can further decompose into more stable LiNO$_3$ and Li$_3$N. Therefore, complete salt degradation can be achieved either by reducing the salt concentration to ultralow levels or by elevating the temperature. A notable trend is that the LiFSI salt in the

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Figure 3. a) Cycling performance and b) coulombic efficiency of Li|Li$_4$Ti$_5$O$_{12}$ batteries at 90 °C. Rate performance of Li|Li$_4$Ti$_5$O$_{12}$ batteries at c) room temperature and d) 90 °C.
dilute electrolyte tends to form LiNO$_3$ from complete salt decomposition, while in the higher concentration electrolytes, Li$_3$N is more favored. Importantly, the LiNO$_3$-rich SEI has been evidenced to have a better protective effect on metallic lithium than the Li$_3$N-rich SEI at high temperature, considerably mitigating the lithium metal corrosion and electrolyte consumption. The compact and stable LiNO$_3$-rich SEI brings about the best cyclic and rate performance of the Li|Li$_4$Ti$_5$O$_12$ batteries using the 0.1 M electrolyte at 90 °C. The utilization of dilute electrolyte also holds an advantage in lowering the production cost of electrolytes, which makes it attractive for practical application. We believe our research has provided new insights into regulating the SEI composition and properties via salt concentration and temperature, which will be helpful for the rational designing of LMBs with enhanced electrochemical and safety performance.

4. Experimental Section

Preparation of Electrolytes and Electrodes: All lithium salt (LiFSI) and solvents (DMC, DEC, and EC) were purchased from Sigma-Aldrich and used without purification. All solvents are using predrying molecular sieve for water removal. Electrolytes of different concentrations were prepared by mixing LiFSI with the solvents (DMC:DEC:EC = 1:1:1 vol. ratio) in glove box (H$_2$O, O$_2$ < 1 ppm). The concentration unit M is defined as lithium salt mol to solvent volume. Li$_4$Ti$_5$O$_12$ electrode was prepared by coating the slurry on Cu foil. Strict mass stoichiometric ratio of the slurry is Li$_4$Ti$_5$O$_12$:Super P:polyvinylidene fluoride (PVDF) = 8:1:1. The area capacity of Li$_4$Ti$_5$O$_12$ electrode is about 1.75 mAh cm$^{-2}$.

Electrochemical Measurements: CR2032-type coin cells were assembled in glove box (H$_2$O, O$_2$ < 1 ppm) to evaluate the cyclic performance, rate performance, EIS, and Li$^+$ transference number, respectively, in Li|Li$_4$Ti$_5$O$_12$ and Li|Li cells. Separator (Cellgard) with Al$_2$O$_3$ coating on both side was used. The amount of electrolyte in a coin cell was ≈120 μL to fully wet the separators and electrodes. Li|Li$_4$Ti$_5$O$_12$ cell was cycled in the voltage range of 1–3 V. The cells are charged and discharged at 0.2 °C rate in the first cycle, and then cycled at 1 °C rate. Cells were tested at 90 °C in the high-temperature oven (±1 °C) by Land BA2100A Battery Test System (Wuhan, China). Variable temperature ionic conductivity was tested by a pen conductivity meter with two directly facing Pt electrodes in the high- and low-temperature oven.

Characterization: Viscosity of electrolyte solutions was measured by rheometer at different temperature. The morphology of deposited lithium was observed by scanning electron microscopy (SEM, HITACHI S4800). Deposited lithium samples were from Li|Cu cells (0.5 mAh cm$^{-2}$, 0.5 mA cm$^{-2}$) discharged in different concentration electrolytes at different temperature, which is also used for surface element analysis. Components and contents of elements of SEI film were obtained from XPS (Thermo Scientific, ESCALAB 250Xi). All samples were transferred with a protection box filled with high purity argon gas.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by funding from the Beijing Municipal Science & Technology (grant no. Z191100004719001), Natural Science Foundation of Beijing (grant No. Z2000042), Natural National Science Foundation of China (grant nos. U196420104, 518222311, and U1932220).
Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

Keywords
concentration, electrolyte, LiFSI, lithium metal anode, solid electrolyte interphase, temperature

Received: January 8, 2021
Revised: February 10, 2021
Published online: April 10, 2021