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Original Research

Lithium Stable Flexible Polyethylene Oxide-Based Composite Electrolyte with High Lithium-Ion Conducting NASICON-Type Solid Electrolyte for Lithium Batteries

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Abstract

Solid lithium-ion conducting polymer electrolytes are attractive candidates for battery applications because they are flexible and less flammable, and can be easily prepared as large-sized thin films. However, the room temperature conductivity of conventional polymer electrolytes is relatively low, and detrimental lithium dendrite formation is observed at high current density. In this study, a composite polymer electrolyte of polyethylene oxide (PEO) with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and a high lithium-ion conducting NASICON-type solid electrolyte of $Li_{1.4}Al_{0.4}Ge_{0.2}Ti_{1.4}(PO_4)_3$-0.75 wt.% $LiCl{\cdot}H_2O$ (LAGTP-$LiCl{\cdot}H_2O$) was developed. The electrical conductivity of PEO_{18}LiTFSI-5 wt.% LAGTP-$LiCl{\cdot}H_2O$ was 1.2×10^{-5} S cm^{-1} at 25°C. The cell resistance of 10000 Ω for the Li/PEO_{18}LiTFSI-5 wt.% LAGTP-$LiCl{\cdot}H_2O$/Li cell was decreased to 1700 Ω by the addition of a small amount of liquid plasticizer, tetraethylene glycol dimethyl ether (G4), and 1,2-dimethoxyethane (DME). The

Li/(PEO_{18}LiTFSI-2G4)-5 wt.% LAGTP-LiCl·H_2O -10 wt.% DME/$LiFePO_4$ cell was successfully cycled at room temperature and 0.2 mA cm^{-2}.

Keywords
Battery; high energy density; NASICON-type conductor; polymer electrolyte; polyethylene oxide

1. Introduction

Several high-energy-density advanced batteries, such as lithium metal [1], lithium air [2, 3], lithium sulfur [3, 4], and all-solid-state lithium batteries [5], have been proposed and developed for electrical vehicles (EVs) in the last three decades. Safety and high energy density of the batteries are essential requirements for EVs; therefore, among these advanced batteries, the all-solid-state batteries are attractive due to their safety. All-solid-state lithium batteries with polymer and inorganic solid electrolytes have been developed, including many that have high lithium ion conductivity at room temperature. Aono et al. reported in 1990 that the NASICON type $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) has a high lithium ion conductivity of 7×10^{-4} S cm^{-1} at 25°C [6]. The perovskite type $Li_{0.34}La_{0.51}TiO_{2.94}$ was also reported to have a high lithium ion conductivity of 1.4×10^{-3} S cm^{-1} at 25°C by Inaguma et al. in 1993 [7]. However, these high-conductivity ceramic solid electrolytes are unstable in contact with lithium. A lithium-stable lithium ion ceramic solid electrolyte of garnet-type $Li_7La_3Zr_2O_{12}$ (LLZ) with high conductivity was reported by Weppner and co-workers in 2007 [8]. More recently, a high lithium ion conductivity of 2.5×10^{-2} at 25°C was observed in $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ (LSiPSCl) [5], which is higher than that of the conventional liquid electrolytes employed in lithium-ion batteries. However, this high-conductivity sulfide-based electrolyte is quite hygroscopic and reacts with water to produce H_2S, which is considerably toxic.

Many types of all-solid-state rechargeable lithium batteries with lithium-ion conducting solid electrolytes have been proposed. Bates et al. reported a lithium solid-state battery of Li/phosphorus oxynitride (LiPON)/$LiCoO_2$ in 1993 [9]. LiPON is stable in contact with Li; however, its lithium ion conductivity is around 10^{-6} S cm^{-1} at room temperature, so a thin film of LiPON was used in cells to produce rechargeable batteries that have been used in consumer and medical electronics [10]. These thin-film batteries are pretty stable, although the cell capacity is typically very low (<0.1 mAh cm^{-2}). Weppner and co-workers [11] reported a lithium rechargeable solid electrolyte cell of $Li_4Ti_5O_{12}$/LATP/Li_2MnO_4 in 1999 that was demonstrated at 10 μA cm^{-2} for 10 cycles. Goodenough and co-workers studied a cell with a high lithium ion conductivity, a lithium-stable solid electrolyte cell of Li/LLZ/$LiCoO_2$ in 2016. The cell was tested at 50°C and 0.1 mA cm^{-2} because room temperature tests showed a short-circuit [12]. The cell performance was improved by modification of the electrolyte-electrode interface, and high charge and discharge performance was observed at high temperature [13]. Solid-state rechargeable batteries with high-conductivity sulfide-based electrolytes have been extensively developed for EVs by motor companies. Kanno et al. reported that a $Li_4Ti_5O_{12}$/LSiPSCl/$LiCoO_2$ cell could be cycled at a high current density of 1.2 mA cm^{-2} at 25°C [5]. Further technical advances in the power density and production costs of the all-solid-state batteries are thus eagerly anticipated [14].

The lithium polymer electrolyte battery was reported by Armand et al. in 1978 [15]. 3M and Hydro-Quebec developed polyethylene oxide (PEO)-based polymer batteries for EVs in the early 1990s that were operated at high temperature because the room temperature conductivity of the PEO-based polymer electrolyte was very low at 10^{-6} S cm^{-1}; a high conductivity of more than 10^{-4} S cm^{-1} was observed at temperatures higher than 60°C. The large-scale polymer electrolyte batteries that were developed experienced cell short-circuiting incidents that resulted in fires. The short-circuit is due to lithium dendrite formation during the charging process. To improve the room temperature conductivity of the polymer electrolytes and suppress lithium dendrite formation, many additives, such as less flammable ionic liquids including poly(vinylidenefluoride)-hexafluoropropane [16] and tetraethylene glycol dimethyl ether (G4) [17], and lithium ion conducting solid electrolytes such as LLZ [18] and LATP [19] have been added to the PEO-based electrolytes. A high lithium ion conductivity of more than 10^{-4} S cm^{-1} at 25°C was reported for a composite of PEO-Li$(CF_3SO_2)_2N$ (LiTFSI)-LLZ [18].

Lithium metal is the most attractive anode for batteries because of its high specific capacity (3861 mAh g^{-1}) and low negative potential (-3.04 V vs. NHE). However, lithium dendrite growth during lithium deposition leads to serious safety problems and poor cycling performance. Many investigations on lithium dendrite formation in lithium conducting polymer electrolytes at high temperatures have been published, although there are few publications on dendrite formation at room temperature [20, 21]. Bag et al. [22] reported the cycle performance for Li deposition and stripping at 0.2 mA cm^{-2} with a polyvinylidene fluorite (PVDF)-$Li_{0.5}La_{2.5}Ba_{0.5}ZrTaO_{12}$ (LLBZTO) composite electrolyte, where the electrical conductivity of $PVDF_4$LiTFSI-2 wt.% LLBZTO was 3.3×10^{-4} S cm^{-1} at 20°C. The symmetrical lithium cell could be cycled only for 30 h at 0.2 mA cm^{-2} and 0.1 mAh cm^{-2}. The addition of 0.25 wt% LiF significantly improved the cycle performance.% LiF to the composite electrolyte; the LiF-modified composite electrolyte was successfully cycled more than 800 h at 0.2 mA cm^{-2} and 25°C. Fan et al. [23] also reported excellent lithium deposition and stripping performance for a composite electrolyte of salt–rich PEO and $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (LLZTO). The composite electrolyte of PEO_6LiTFSI-10 wt.% LLZTO showed a high electrical conductivity of 2.13×10^{-4} S cm^{-1} at 25°C and superior interface stability with lithium metal, even at a high current density of 2 mA cm^{-2}. However, this composite electrolyte contains approximately 50 wt.% of LiTFSI, an expensive salt, and the reported thickness of the composite electrolyte was 200 µm. It may be challenging to prepare a thin film of the salt-rich PEO electrolyte. We have focused on the development of a room temperature operation, high lithium ion conducting, and lithium dendrite formation-free flexible polymer electrolyte. We previously reported [24] a composite polymer electrolyte of (PEO_{18}TFSI-2G4)-10 wt.% LLZTO-10 wt.% 1,2-dimethoxyethane (DME), which exhibited a high conductivity of 6×10^{-4} S cm^{-1} at 25°C and excellent cycle performance at 0.2 mA cm^{-2} and 0.2 mAh cm^{-2} at 25°C. In the present study, composite polymer electrolytes with a high lithium ion conducting solid electrolyte of PEO_{18}LiTFSI-$Li_{1.4}Al_{0.4}Ge_{0.2}Ti_{1.4}(PO_4)_3$-0.75 wt.% LiCl·$H_2O$ (LAGTP-LiCl·H_2O) were examined. $Li_{1.4}Al_{0.4}Ti_{0.6}(PO_4)_3$-xLiCl·$H_2O$ was reported to have a high lithium ion conductivity of 9.2×10^{-3} S cm^{-1} at 25°C by Imanishi and co-workers [25]. The room temperature full cell performance of a cell with the flexible composite solid polymer electrolyte was also examined.

2. Experimental

The NASICON-type lithium ion conducting solid electrolyte $Li_{1.4}Al_{0.4}Ge_{0.2}Ti_{1.4}(PO_4)_3$ (LAGTP) was prepared by a previously reported sol-gel method using citric acid [26]. Stoichiometric amounts of $Ti(OC_4H_9)$ (Aldrich) and $Ge(OC_2H_5)$ (Aldrich) were dissolved in ethylene glycol, added to a 0.2 M aqueous solution of citric acid, and then stirred continuously with a magnetic stirrer at 100°C for 12 h to obtain a homogenous solution. After preparation of the gel was completed, stoichiometric amounts of $Li(NO_3)$, $Al(NO_3)_3{\cdot}9H_2O$, and $NH_4H_2PO_4$ (Nacalai Tesque) were added to the gel solution. The molar ratio of citric acid to ($Li^+ + Al^{3+} + Ge^{4+} + Ti^{4+}$) was 4:1. After a homogenous solution was formed, the gel was kept at 170°C for 4 h to allow the evaporation of water and to promote esterification and polymerization. The gel was then heated at 500°C for 4 h. The black product with residual carbon was ground to a uniformly fine powder with an agate mortar and pestle, and then heated at 900°C for 5 h. The LAGTP powder was high-energy mechanically milled (Fritsch Planetary Micro Mill), and the fine powder was isostatically pressed into a pellet form at a pressure of 150 MPa and sintered at 900°C for 6 h. The sintered pellets were immersed in a LiCl-saturated aqueous solution at 50°C for one week to obtain LAGTP-$LiCl{\cdot}H_2O$. The content of $LiCl{\cdot}H_2O$ of 0.75 wt.% was estimated from the weight change of the pellets before and after. The pellets were milled again using the high-energy mechanical mill in open air. The LAGTP-$LiCl{\cdot}H_2O$ was transferred to an Ar-filled glove box just before set-up of the Li/PEO_{18}LiTFSI-2G-LATP-$LiCl{\cdot}H_2O$-DME/$LiFePO_4$ cell.

PEO_{18}LiTFSI-(LAGTP-$LiCl{\cdot}H_2O$) composite electrolytes were prepared by a casting method. PEO (Sigma Aldrich, $M_w = 6 \times 10^5$) and LiTFSI (Wako Chemical, Japan) were dried overnight under vacuum at 50°C and 160°C, respectively. PEO, LiTFSI, and LAGTP-$LiCl{\cdot}H_2O$ powder were added to acetonitrile and magnetically stirred for 24 h. Various weight percentages of LAGTP-$LiCl{\cdot}H_2O$ were dispersed in solution to prepare various composite electrolytes. The solution was cast on a Teflon mold. These procedures were carried out in an Ar-filled glove box. The solvent was evaporated slowly at room temperature under nitrogen gas flow, and then dried at 110°C for 4 h. The diameter and thickness of the composite electrolytes PEO_{18}LiTFSI-(LAGTP-$LiCl{\cdot}H_2O$) were 1 cm and 0.02 cm, respectively.

Electrical conductivity measurements of the composite electrolytes were performed using a frequency response analyzer (Solartron 1250) in the frequency range of 0.1 Hz to 1 MHz and the temperature range of 25-80°C. Samples in coin-type cells with stainless electrodes were heated up to 80°C and then cooled down to room temperature to produce a good contact between the electrode and the composite electrolyte. A full Li/[$(PEO)_{18}$LiTFSI-2G-5 wt.%(LAGTP-$LiCl{\cdot}H_2O$)]-10 wt.% DME/$LiFePO_4$ cell was tested in a 2023-type coin cell. The $LiFePO_4$ cathode was prepared by mixing $LiFePO_4$, carbon, and the composite electrolyte in a weight ratio of 8:1:1 with a 1.30 mg charge of $LiFePO_4$. $LiFePO_4$ was purchased from Housen Co., Japan. The cells were placed in an Ar-filled glove box.

3. Results and Discussion

Figure 1 shows impedance profiles measured at 25°C of LAGTP immersed in a saturated aqueous solution of LiCl for one week at 50°C, where the content of LiCl in LAGTP was 0.76 wt.%. The conductivity measured in the ambient atmosphere is as high as 4.33×10^{-3} S cm^{-1} at 25°C, which is approximately 5 times higher than that of pure LAGTP [26] and more than one order higher than the commercialized NASICON-type solid lithium ion conductor of $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ (LATP Ohara)

from Ohara Co. [27]. The high electrical conductivity of LAGTP-LiCl·H_2O is due to the high conductivity of the grain phase of LiCl·H_2O [25].

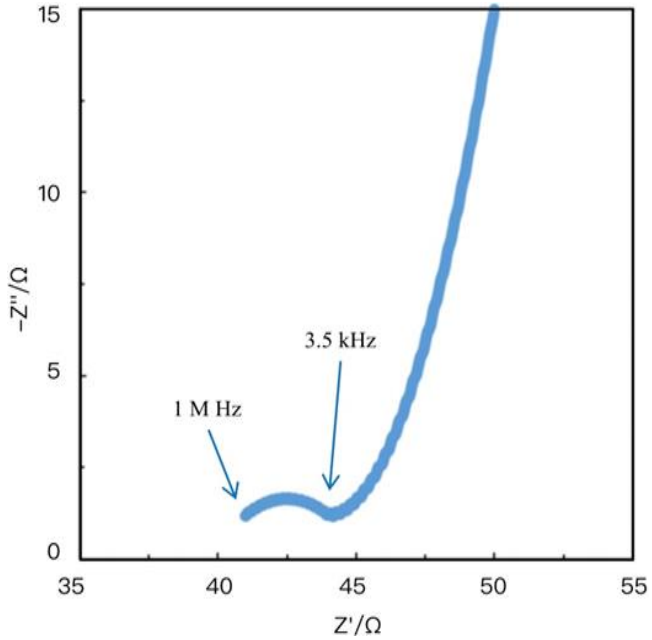

Figure 1 Impedance profile of LAGTP-LiCl·H_2O at 25°C.

The flexible composite polymer electrolyte of PEO_{18}LiTFSI and the high lithium-ion conducting solid electrolyte of LAGTP-LiCl·H_2O were examined. Figure 2 shows impedance profiles of the PEO_{18}LiTFSI-x(LAGTP-LiCl·H_2O) composite electrolytes at 25°C for various x, the conductivity vs. x curve, and the temperature dependence of the electrical conductivity, where the thickness of the composite electrolytes was around 200 µm. The conductivity of 1.42 × 10^{-5} S cm^{-1} for PEO_{18}LiTFSI-10 wt.% (LAGTP-LiCl·H_2O) is higher than that of 7.5 × 10^{-6} S cm^{-1} at 25°C for PEO_{18}LiTFSI-10 wt.% LLZTO [24], 3 × 10^{-6} at 30°C for $PEO_{15}LiCF_3SO_3$-10 wt.% LATP [28] and 3 × 10^{-6} S cm^{-1} at 25°C for PEO_{18}LiTFSI [24]. The activation energy for conduction of 103 kJ mol^{-1} for PEO_{18}LiTFSI-10 wt.% (LAGTP-LiCl·H_2O) at room temperature is slightly higher than that of 96.5 kJ mol^{-1} for PEO_{18}LiTFSI-10 wt.% LLZ [24]. The activation energy was estimated from the Arrhenius equation of $\sigma = A \cdot \exp(-E/RT)$, where σ is the conductivity, A is the pre-exponential factor, E is the activation energy, R is the gas constant, and T is the absolute temperature.

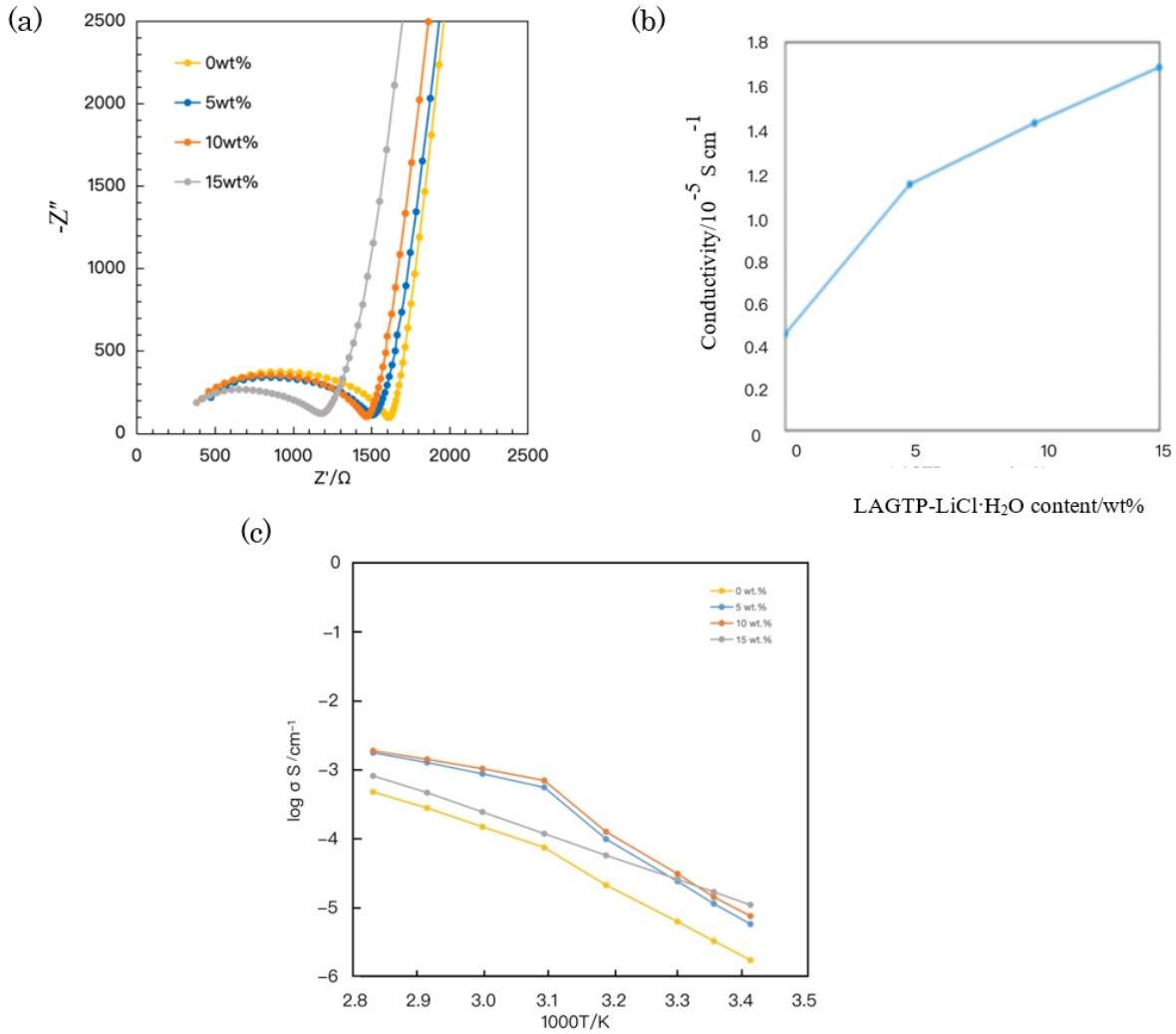

Figure 2 (a) Impedance profiles of $PEO_{18}LiTFSI$-x(LAGTP-LiCl·H_2O) at 25°C, (b) the electrical conductivity (σ) of $PEO_{18}LiTFSI$-x(LAGTP-LiCl·H_2O) vs. LAGTP-LiCl·H_2O content curve, and (c) temperature dependence of the conductivity of $PEO_{18}LiTFSI$-x(LAGTP-LiCl·H_2O).

Imanishi et al. reported that Ohara LATP is unstable in contact with lithium at 80°C [29]. The initial cell resistance of 1000 Ω for Li/Ohara LATP/Li at 80°C increased to 8 × 10^6 Ω after one week. However, Yu and Manthiram reported that the Li/$PEO_{15}LiCF_3SO_3$-50 wt.% $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP)/$LiFePO_4$ cell could successfully operate at 60°C [28]. Similar full cell performance for the PEO-based electrolyte and LATP composite electrolytes was reported by Ban et al. [30] and Yang et al. [31]. These cells were also operated at 60°C, and the composite electrolytes were stable in contact with lithium. However, no results for the stability of the composite electrolyte with lithium at room temperature were reported. The PEO-based electrolyte may protect against direct contact of LATP with lithium. We have investigated the stability of the $PEO_{18}LiTFSI$-x wt.% (LAGTP-LiCl·H_2O) (x = 5 and 10) composite electrolytes in contact with lithium at room temperature. Figure 3 shows the impedance profiles of the Li/$PEO_{18}LiTFSI$-5 wt.% (LAGTP-LiCl·H_2O)/Li and Li/$PEO_{18}LiTFSI$-10 wt.% (LAGTP-LiCl·H_2O)/Li cells measured at 25°C with the equivalent circuits shown in the inset. The impedance profiles of the cell have two semicircles. The intercept of the high-frequency semicircle with the real axis at high frequency is the bulk resistance of the composite electrolyte (R_1). The

semicircle in the high frequency range of 1 MHz-2~3 kHz corresponds to the grain boundary resistance (R_2) with a parallel constant phase angle (CPE_2) and a solid electrolyte interphase (SEI; R_3) with a parallel constant angle (CPE_3), and those in the low frequency range correspond to the charge transfer resistance (R_4) with a parallel constant angle (CPE_4) [32]. The parts of the SEI and the grain boundary phase were integrated in this composite electrolyte—the high SEI resistance of the composite electrolyte with 10 wt.% LAGTP-LiCl·H_2O may be due to the formation of a decomposition product of LAGTP-LiCl·H_2O with lithium due to the direct contact of LAGTP-LiCl·H_2O and lithium—the initial cell resistance of around 5000 Ω for the composite with 5 wt.% LAGTP-LiCl·H_2O increased with the storage period, and a steady cell resistance of around 10000 Ω was observed—the cell with 10 wt.% LAGTP-LiCl·H_2O showed a high cell resistance of more than 40000 Ω.

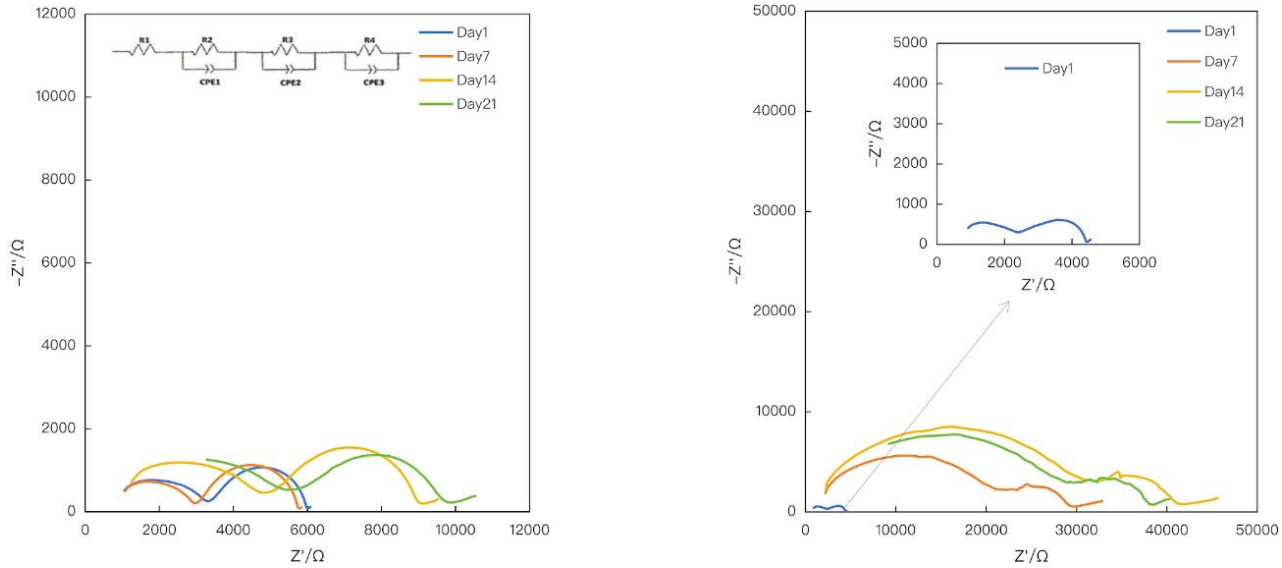

Figure 3 Impedance profiles of (a) Li/PEO_{18}LiTFSI-5 wt.% LAGTP-LiCl/Li and (b) Li/PEO_{18}LiTFSI-10 wt.% LAGTP-LiCl/Li at 25°C for various storage periods.

To reduce the resistance of the Li/polymer lithium-ion conductors/Li cell, plasticizers such as G4 [33], succinonitrile (SN) [34], and DME [24] have been introduced into the polymer electrolytes. In this study, we examined the addition of G4 and DME into PEO_{18}LiTFSI-5 wt.% LAGTP-LiCl·H_2O. The electrical conductivity of (PEO_{18}LiTFSI-2G4)-5 wt.% LAGTP-LiCl·H_2O-10 wt.% DME was considerably increased by the additions of G4 and DME to 10^{-3} S cm^{-1} at 25°C. The impedance profiles of Li/(PEO_{18}LiTFSI-2G)-5 wt.% LAGTP-LiCl·H_2O-10 wt.% DME/Li at 25°C are shown in Figure 4 for various storage periods. The impedance profiles show only one semicircle, which may correspond to the SEI and charge transfer resistance. A steady cell resistance of around 1700 Ω was observed; the diameter of the lithium electrode was 10 mm, and the thickness of the film was around 0.2 mm. The composite electrolyte with plasticizers of G4 and DME is flexible, as shown in Figure 4(b). The stress vs. strain curves of (PEO_{18}LiTFSI-2G4)-5 wt.% LAGTP-LiCl·H_2O are shown in Figure 4(c). The tensile strength of 0.05 M Pa is considerably lower than that of 0.78 M Pa for PEO_{18}LiTFSI-10 wt.% $Li_7La_3Zr_2O_{12}$ and lower than that of 0.127 M Pa for PEO_{18}LiTFSI-2G4-10 wt.% LLZ-10 wt.% DME [24].

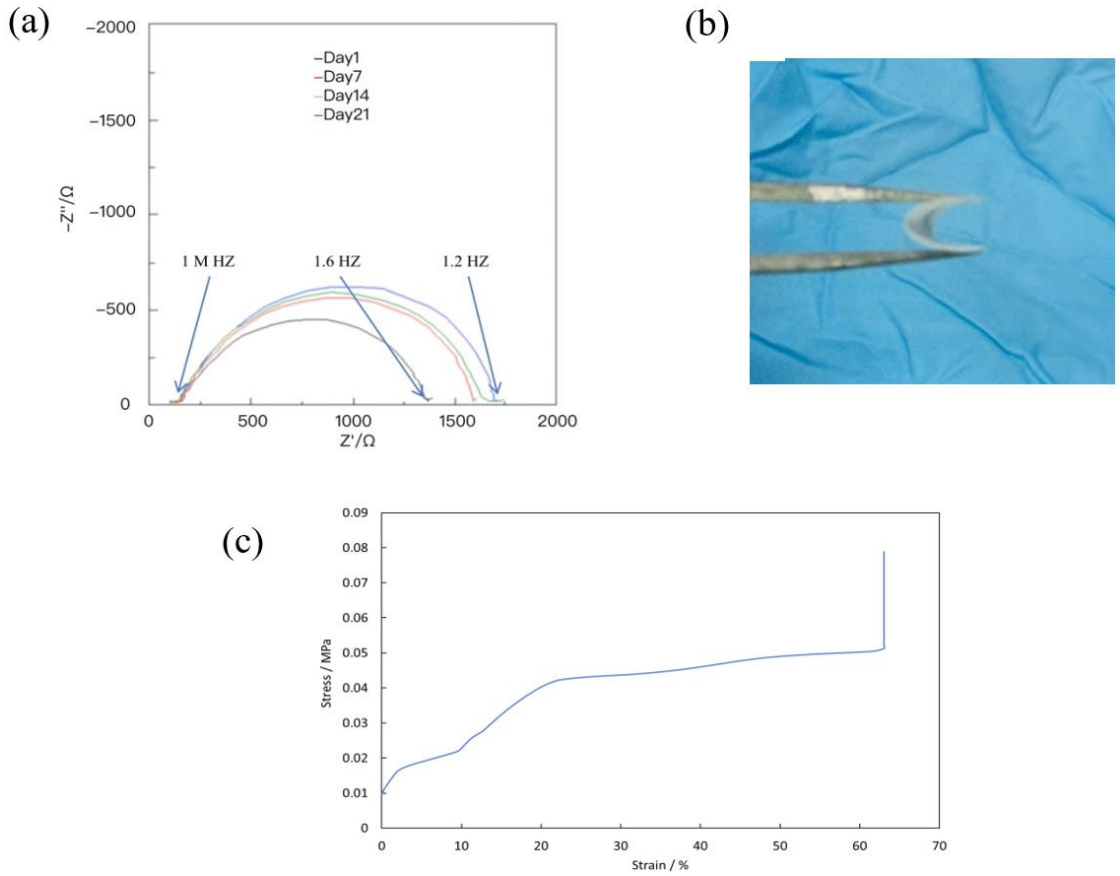

Figure 4 (a) Impedance profiles of Li/(PEO_{18}LiTFSI-2G4)-5 wt.% (LAGTP-LiCl·H_2O)-10 wt.% DME/Li for various storage periods at 25°C, (b) a photograph of the (PEO_{18}LiTFSI-2G4)-5 wt.% (LAGTP-LiCl)-10 wt.% DME film and (c) stress-strain curve for (PEO_{18}LiTFSI-2G4)-5 wt.% (LAGTP-LiCl)-10 wt.% DME.

A composite polymer electrolyte for lithium battery applications should have a stable electrochemical potential window, excellent lithium deposition and stripping performance, along with high lithium ion conductivity. Figure 5 shows a linear sweep voltammogram measured at 25°C for Li/(PEO_{18}LiTFSI-2G4)-5 wt.% (LAGTP-LiCl·H_2O)-10 wt.% DME/stainless steel (SS) with a scan rate of 1 mV s^{-1}. The composite electrolyte is stable up to around 4.2 V, which is comparable to that for PEO_{18}LiTFSI-2G4-10 wt.% LLZ-10 wt.% DME [24].

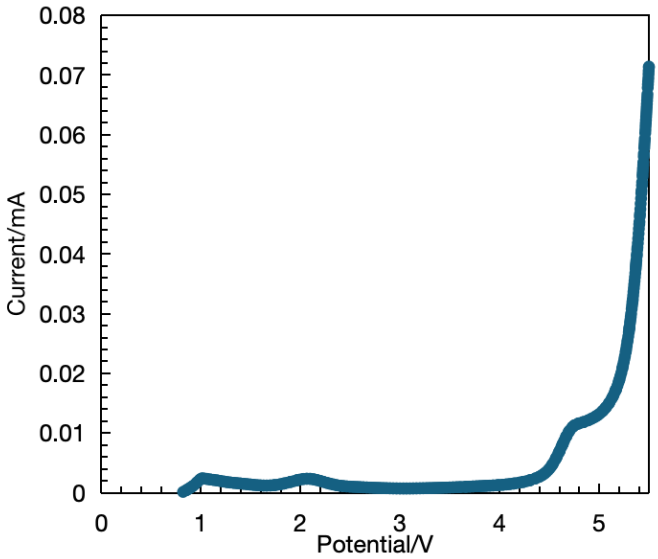

Figure 5 Linear sweep voltammogram for Li/(PEO_{18}LiTFSI-2G4)-5 wt.% (LAGTP-LiCl·H_2O)-10 wt.% DME/SS measured at 25°C with a scan rate of 1 mV s^{-1}.

The room temperature lithium electrode performance of the conventional polymer electrolytes is not at an acceptable level, because of a high lithium deposition and stripping overpotential and the ease of lithium dendrite formation [21]. The lithium electrode performance of the PEO based electrolytes has been mainly investigated at high temperatures such as 70°C [34], 60°C [28, 30, 35] and 55°C [36]; however, there has been only a few reports of the Li/polymer electrolyte/Li cell performance at room temperature [23, 24, 37, 38]. Table 1 summarizes the cyclic performance of Li/composite polymer electrolyte/Li at 25°C. Fan et al. reported lithium deposition and stripping cycle performance for polymer/salt of PEO_6LiTFSI and $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ nanofiber (LLZTO) composite electrolyte. The Li/PEO_6LiTFSI-10 wt.% LLZTO/Li cell was cycled for over 450 h at 0.1 mA cm^{-2} with an overpotential of 0.02 V at 25°C [23]. Fu et al. [37] reported an excellent lithium cyclic performance for the composite electrolyte of PEO_{18}TFSI-3D garnet nanofiber networks, where electrospinning of polyvinylpyrrolidone polymer mixed with LLZTO prepared the 3D garnet nanofiber networks. The composite polymer electrolyte showed an excellent lithium deposition and stripping cyclic performance at 0.5 mA cm^{-2} and 0.25 mAh cm^{-2}. The preparation of the large-sized composite electrolyte is not convenient. Abe et al. reported that Li/(PEO_{18}LiTFSI-2G)-10 wt.% LLZTO-5 wt.% DME/Li was cycled over 900 h at 0.2 mA cm^{-2} with an overpotential of 0.4 V [24]. In this study, the room temperature lithium electrode performance of the Li/Li symmetrical cell with the composite electrolyte was examined. Figure 6 shows the temperature dependence of the electrical conductivity of (PEO_{18}LiTFSI-2G4)-5 wt.% (LAGTP-LiCl·H_2O)-10 wt.% DEM, along with PEO_{18}LiTFSI-5 wt.% LAGTP-LiCl·H_2O. The activation energy for conduction at near room temperature of 81 kJ mol^{-1} of the composite with G4 and DME is lower than that of 101 kJ mol^{-1} of the composite without G4 and DME.

Table 1 Ionic conductivity and cyclic performance of Li/composite electrolyte/Li.

Electrolyte	Ionic conductivity at 25°C	Li/electrolyte/ Li cell cyclic life	Ref.
$PVDF_4LiTFSI$-2 wt.% LLBZTO	3.3×10^{-4}	0.2 mA cm^{-2}, 0.1 mAh, 30 h	[22]
$PEO_{18}LiTFSI$-2G-10 wt.% LLZ	3.25×10^{-4}	0.2 mA cm^{-2}, 0.2 mAh cm^{-2}, 600 h	[24]
$PEO_6LiTFSI$-10 wt.% LLZ	2.13×10^{-4}	0.1 mA cm^{-2}, 0.1 mAh^{-2}, >450 h	[23]
$PEO_{18}LiTFSI$-10 wt.% 3D LLZ nanofiber	2.5×10^{-4}	0.5 mA cm^{-2}, 0.25 mAh cm^{-2}, >1000 h	[37]
$PEO_{15}LiCF_3SO_3$-25 wt.% LATP Ohara	1.3×10^{-4}	0.2 mA cm^{-2}, 0.1 mAh cm^{-2}, >100 h	[28]
$PEO_{18}LIFSI$-2G-5 wt.% LAGTP-$LiCl{\cdot}H_2O$-10 wt.% DEE	1.2×10^{-4}	0.2 mA cm^{-2}, 0.2 mA h cm^{-2}, >600 h	This study

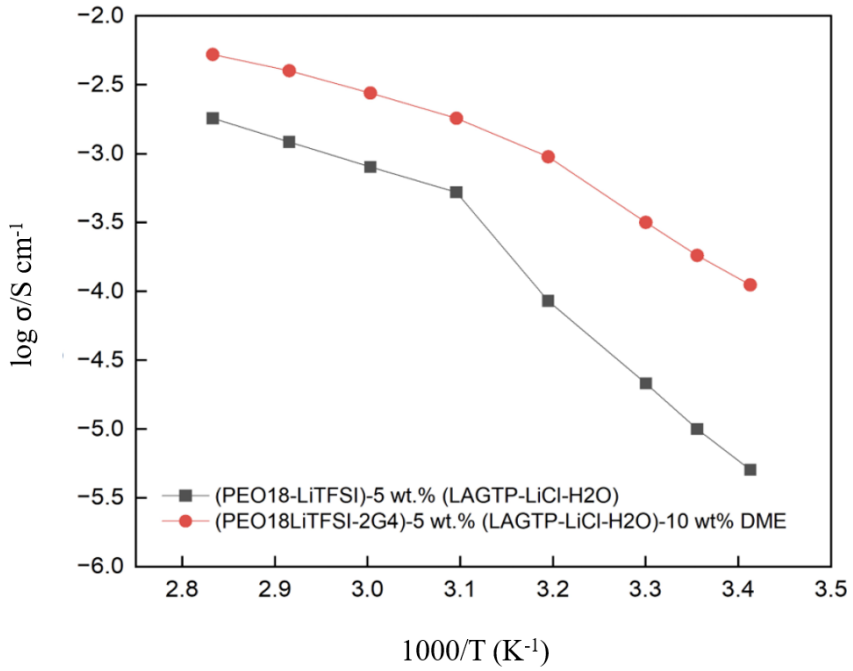

Figure 6 Temperature dependence of the electrical conductivity of ($PEO_{18}LiTFSI$-2G4)-5 wt.% (LAGTP-$LiCl{\cdot}H_2O$)-10 wt.% DME and $PEO_{18}LiTFSI$-5 wt.% LAGTP-$LiCl{\cdot}H_2O$.

Figure 7 shows the cycle performance of the Li/($PEO_{18}LiTFSI$-2G4)-5 wt.% (LAGTP-$LiCl{\cdot}H_2O$)-10 wt.% DME/Li cell at 0.2 mA cm^{-2} and 25°C for 1 h polarization and 10 min rest. Steady cycle performance was observed for more than 600 h. The charge and discharge potentials were around 0.37 V at 0.2 mA cm^{-2}, respectively.

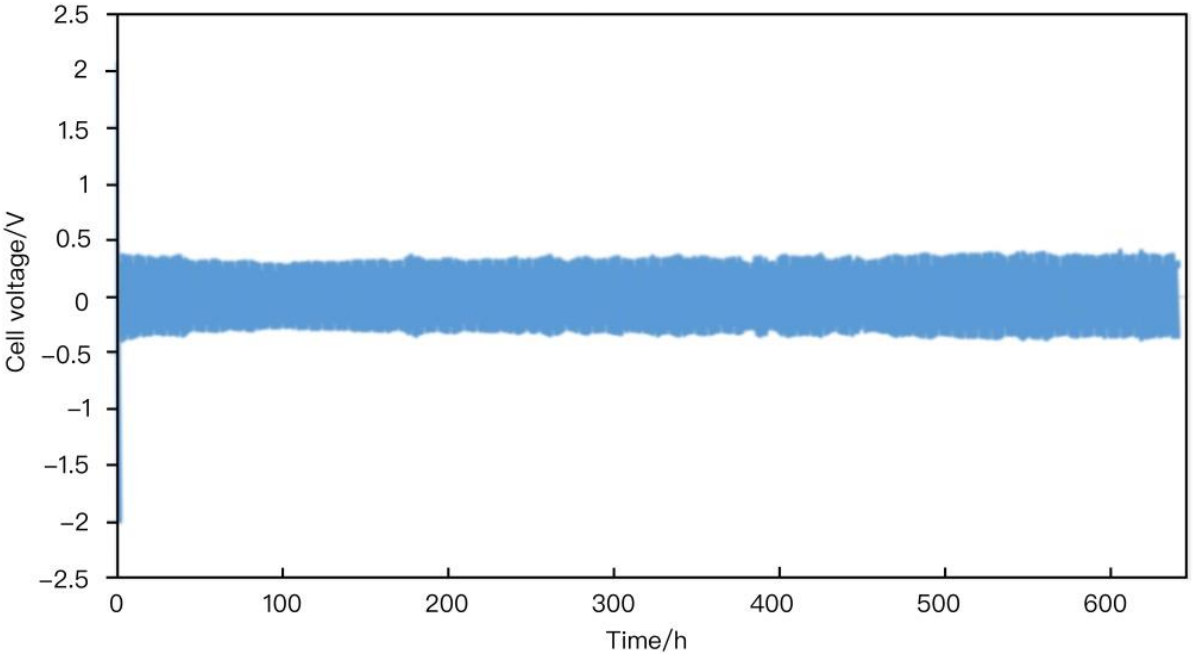

Figure 7 Cycle performance of Li/(PEO_{18}LiTFSI-2G4)-5 wt.% (LAGTP-LiCl·H_2O)-10 wt.% DME/Li at 0.2 mA cm^{-2} and 25°C.

The full cell performance of Li/(PEO_{18}LiTFSI-2G4)-5 wt.% (LAGTP-LiCl·H_2O)-10 wt.% DME. $LiFePO_4$ was examined at 25°C. Figure 8(a) shows the cycle performance of the Li/(PEO_{18}LiTFSI-2G4)-5 wt.% (LAGTP-LiCl·H_2O)-10 wt.% DME/$LiFePO_4$ cell at 0.2 mA cm^{-2} and 25°C, where the mass of $LiFePO_4$ in the cathode was 1.3 mg. The charge and discharge cut-off voltages were 4.2 V and 2.5 V, respectively. Figure 8(b) shows that the cell exhibited better capacity retention and high coulombic efficiency for the charge and discharge capacity at 0.2 mA cm^{-2} and 25°C.

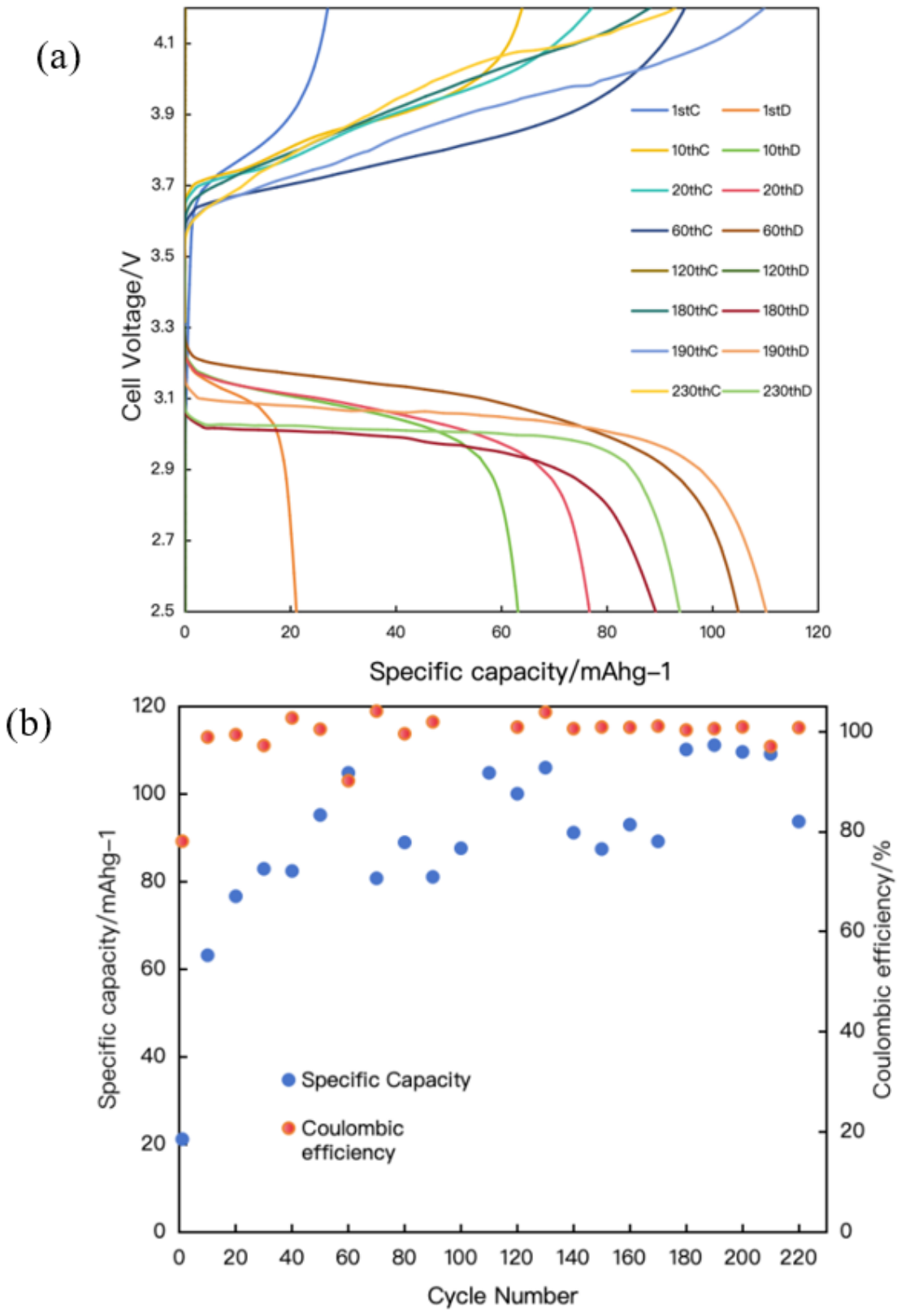

Figure 8 (a) the whole cell cycle performance at 0.2 mA cm^{-2} and (b) capacity retention and coulombic efficiency with cycle number at 0.2 mA cm^{-2} of Li/(PEO_{18}LiTFSI-2G4)-5 wt.% (LAGTP-LiCl·H_2O)-10 wt.% DME/$LiFePO_4$ at 25°C.

4. Conclusion

A flexible lithium-stable PEO-based polymer electrolyte of PEO_{18}LiTFSI-5 wt.% (LAGTP-LiCl·H_2O) was developed. The electrical conductivity of the composite polymer electrolyte was 1.2×10^{-5} S cm^{-1} at 25°C. The high lithium ion conducting LAGTP-LiCl·H_2O filler effectively enhanced the conductivity of PEO_{18}LiTFSI. The addition of G4 and DME reduced the interface resistance between Li and the composite electrolyte. The Li/(PEO_{18}-LiTFSI-2G4)-5 wt.% (LAGTP-LiCl·H_2O)-10 wt.% DME/Li cell had stable cycle performance for more than 600 h at 0.2 mA cm^{-2} for 1 h polarization at 25°C. The whole cell of Li/(PEO_{18}-LiTFSI-2G4)-5 wt.% (LAGTP-LiCl·H_2O)-10 wt.% DME/$LiFePO_4$ was successfully cycled at 0.2 mA cm^{-2} and 25°C for more than 200 cycles.

Author Contributions

Z.W. investigation, formal analysis; D.M. and S.T formal analysis; Y.T. review and editing; O.Y. supervision, writing, & editing; N.I. supervision, project administration, review & editing.

Competing Interests

The authors have declared that there are no competing interests.

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