



Semiconductor TiO₂ ceramic filler for safety-improved composite ionic liquid gel polymer electrolytes

Xiaona Pan^{1,2} · Qingjie Hou³ · Lei Liu⁴ · Jinqiu Zhang¹ · Maozhong An¹ · Peixia Yang¹

Received: 6 September 2020 / Revised: 9 November 2020 / Accepted: 17 November 2020 / Published online: 23 February 2021
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Abstract

Gel polymer electrolytes are one of the candidates for solid electrolytes to solve safety issues and improve the energy density of solid-state lithium batteries. Gel polymer electrolyte has high ionic conductivity at room temperature ($\sim 10^{-3}$ S cm⁻¹), but its mechanical properties are poor. Herein, we prepared a series of composite gel polymer electrolytes by N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide, poly(vinylidene fluoride-hexafluoropropylene), LiTFSI, and various inorganic fillers. The addition of 5 wt% TiO₂ can not only increase the ionic conductivity of gel polymer electrolytes but also improve the mechanical properties of gel polymer electrolytes. Besides, as a semiconductor, the TiO₂ has safety risk when uses in composite gel polymer electrolyte. TiO₂-ILGPE safety is investigated by cyclic voltammetry and battery performance. Additionally, TiO₂-ILGPE displays a perfect flame-retarding ability, and TiO₂ would not be reduced by the lithium metal anode.

Keywords Gel polymer electrolytes · Solid-state lithium metal batteries · Safety issues · Inorganic oxide particles · Mechanical property

Introduction

Lithium-ion batteries are widely used in electronic devices, hybrid vehicles, and vehicles [1–3]. However, lithium-ion batteries have reached their bottleneck, in which energy density and power density are limited by the electrode materials [4, 5]. Solid-state lithium metal batteries are one of the candidate's electrolytes for achieving high energy density [6, 7]. Solid-state lithium metal batteries use lithium metal as the electrode, and its theoretical capacity is ten times than that of the

graphite. Furthermore, solid-state lithium metal batteries use solid electrolytes to replace commercial organic liquid electrolytes, which can solve the safety issues.

Generally, solid-state electrolytes are classified into inorganic solid-state electrolytes, polymer electrolytes, and gel polymer electrolytes [8, 9]. Inorganic solid electrolytes are rigid, which causes interfacial contact issues and extremely high interfacial resistance [10–12]. Polymer electrolytes have low ionic conductivity at room temperature ($< 10^{-4}$ S cm⁻¹) [13, 14]. Gel polymer electrolytes are prepared by adding a plasticizer to polymer electrolytes to improve the ionic conductivity, where ionic conductivity is about 10^{-3} S cm⁻¹ [15–19]. However, the mechanical properties of gel polymer electrolytes are poor, and filling with inorganic particles can improve that. It is a common method to improve the mechanical properties of polymer electrolytes by adding inorganic particles. Therefore, many inorganic particles have been composited into polymer electrolytes to improve mechanical properties and electrochemical performance [20–24]. Tambelli et al. [25] reported that the highest room temperature ionic conductivity of PEO-Al₂O₃ composite polymer electrolytes was less than 10^{-4} S cm⁻¹. Xiao et al. [25] fabricated a high-performance composite polymer electrolyte doped with Li_{0.1}Ca_{0.9}TiO₃ particles with a high room temperature ionic conductivity of 3.947 mS cm⁻¹, where the as-prepared CPE

✉ Peixia Yang
yangpeixia@hit.edu.cn

¹ MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China

² Key Laboratory of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, and State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

³ School of Environmental Science and Engineering, Shandong University, Qingdao 266237, China

⁴ Tianjin Key Laboratory of Evaluation Technology for Electric Vehicles, China Automotive Technology and Research Center Co., Ltd. (CATARC), Tianjin 300300, China

membranes needed to be immersed into an organic electrolyte for 0.5 h before the test. Liu group [26] used $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ nanowires as fillers to enhance the ionic conductivity of polymer electrolyte, and the ionic conductivity was 0.24 mS cm^{-1} at room temperature. Others [27–32] reported inorganic particle composite polymer electrolytes, where the room temperature ionic conductivity was around $< 10^{-4} \text{ S cm}^{-1}$.

In our previous work [33], we prepared a high-performance ionic liquid gel polymer electrolyte (ILGPE), which exhibited good battery performance. We utilized an ionic liquid as polymer electrolytes plasticizer to enhance their ionic conductivity, and the optimized ILGPE had a high ionic conductivity of 1.3 mS cm^{-1} at 23°C . To improve the ionic conductivity and mechanical properties of the optimized ILGPE, we combined ILGPE and TiO_2 , MgO , SiO_2 , ZrO_2 , CeO_2 , NiO , Bi_2O_3 , and Al_2O_3 inorganic electrolytes to fabricate composite gel polymer electrolytes, and the properties of these electrolytes were tested. The interaction of TiO_2 in ILGPE was investigated, and the safety of TiO_2 -ILGPE was discussed.

Methods and materials

Fabrication of composite gel polymer electrolytes The preparation of ionic liquid gel polymer electrolytes (ILGPE) and composite ionic liquid gel polymer electrolytes (CILGPE) filled with inorganic particles (TiO_2 , MgO , SiO_2 , ZrO_2 , CeO_2 , NiO , Bi_2O_3 , and Al_2O_3 , 99.8%, Aladdin) followed a previous report [33]. N-Methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13TFSI, Lanzhou Greenchem ILs) ionic liquid, LiTFSI (98+%, Alfa Aesar), and poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP, MW ~ 455,000, Sigma) were dissolved in N-methyl-2-pyrrolidone (NMP) with the weight ratio of 3:1:1, and then vigorously stirred to obtain a homogenous electrolyte slurry at room temperature. For $x\text{wt}\%$ CILGPE ($x = 0\sim 20$), $x \text{ g}$ inorganic particles were dispersed in the NMP solvent by ultrasonic treatment for 15 min and then mixed with the 100 g ILGPE slurry. Finally, the resulting slurry was cast onto a glass plate and dried in a vacuum oven for 48 h at 80°C . The dried polymer electrolytes were transferred to an Ar-filled glovebox and then punched into round disks with a diameter of 19 mm.

Ionic conductivity of electrolytes Ionic conductivity of the polymer electrolytes was tested by potentiostat electrochemical impedance spectroscopy (EIS) on the Princeton Applied Research VestaSTAT4 by using a stainless steel/stainless steel (SS/SS) structure in a coin cell as previously reported [15, 33]. The frequency ranged from 100 kHz to 1 Hz with an AC amplitude of 5 mV. The bulk resistance (R_b) of the polymer electrolytes was obtained by the equivalent circuit of EIS Nyquist plots; the area of the polymer electrolyte was S (cm^2); the thickness (L) of the polymer electrolyte was

measured by a digital thickness gauge (Mitutoyo 547-526S 0–12 mm), and the ionic conductivity (σ) was calculated using the following equation:

$$\sigma = \frac{L}{R_b S} \quad (1)$$

Mechanical test Tensile specimens of the polymer electrolytes were cut off in the form of “dogbone shaped” strips from the molded plate (the size of the specimens was a length of 9 mm, the width of 3.5 mm, and thickness of around 200–300 μm). The measurements were performed on a TA Instruments DMA Q800 V21.2 with a test speed of 1.5 N min^{-1} .

Cell performance testing Five wt% TiO_2 -ILGPE as the working electrode, Li-metal as the counter electrode, and the reference electrode, glass fiber as the separator, and 1 M LiPF_6 EC/DMC ($v/v = 1/1$) as the electrolyte at C/10 and 23°C . The mass loading of the active material (TiO_2) of the working electrode is about 0.09 mg cm^{-2} . The 1C is defined as 335 mAh g^{-1} .

Results and discussions

Ionic conductivity of electrolytes Table S1 shows the ionic conductivity of ILGPE with various inorganic particles with weight percentages of 2.5–20% at 30°C . The highest ionic conductivity of CILGPE shows various weight percentage of inorganic particles. The highest conductivity with optimized composition is shown in Fig. 1.

Figure 1 displays the highest ionic conductivity of inorganic composite ionic liquid gel polymer electrolytes (CILGPE) with their optimized compositions at 30°C .

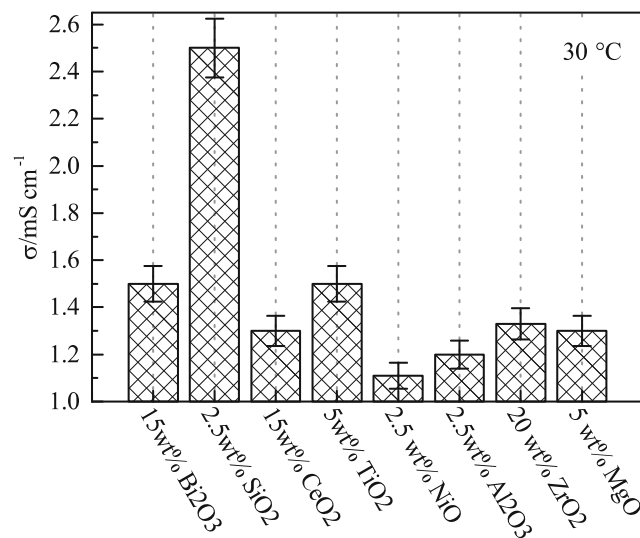
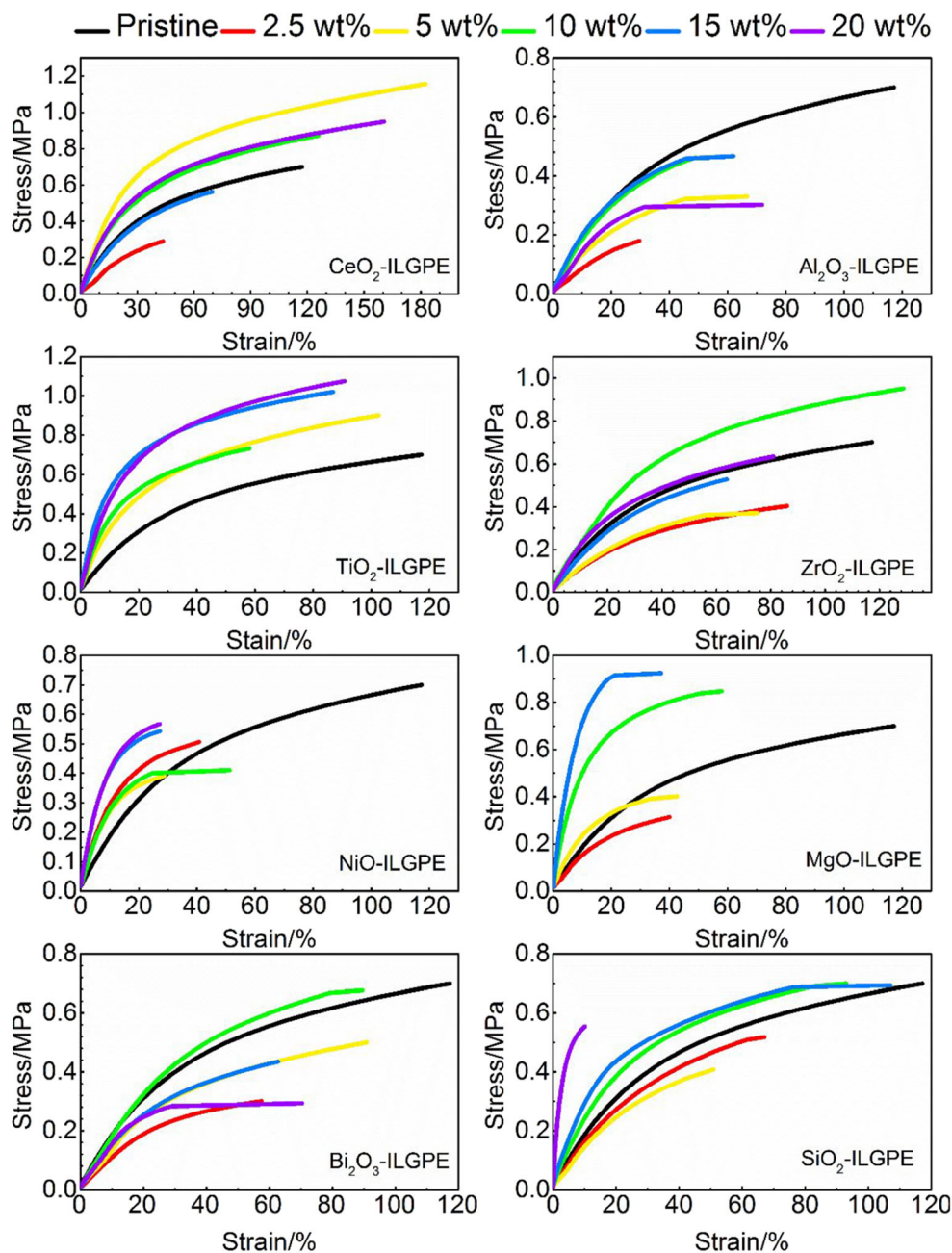


Fig. 1 The optimized composite gel polymer electrolytes and their ionic conductivity at 30°C

As can be observed in Fig. 1, the 2.5 wt% SiO₂-ILGPE has the highest ionic conductivity of 2.5 mS cm⁻¹ at 30 °C, while that of 15% Bi₂O₃-ILGPE and 5 wt% TiO₂-ILGPE is 1.5 mS cm⁻¹ at 30 °C. However, the 2.5 wt% NiO-ILGPE show the lowest ionic conductivity amount of these polymer electrolytes. α-Al₂O₃, selected as a filler in the work, is a lithium-ion nonconductor, and the ionic conductivity of 2.5 wt% α-Al₂O₃-ILGPE is relatively low. The ionic conductivity of 20 wt% ZrO₂-ILGPE and 5 wt% MgO-ILGPE is acceptable. The ionic conductivity of these polymer electrolytes with inorganic particles is ~10⁻³ S cm⁻¹.

Furthermore, there is a sudden increase in ionic conductivity with *x*% addition of inorganic fillers (Table S1). While higher or lower than that concentration of *x*, the ionic conductivity is obviously low. For instance, the ionic conductivity of 2.5 wt% TiO₂-ILGPE and 10 wt% TiO₂-ILGPE is 1.1 mS cm⁻¹ and 0.98 mS cm⁻¹, respectively. The ionic conductivity of polymer electrolytes could exhibit an optimized value with the addition of 5 wt% TiO₂. The results are in agreement with those described in the literature, where a maximum in the ionic conductivity occurs as the increase of the filler concentration [25, 34], followed by a decrease in ionic conductivity values for higher filler weight percentage.

Fig. 2 Tensile test for composite gel polymer electrolytes. Tensile strength was tested five times for each sample to ensure that these results were reproducible



Additionally, the decrease observed in high filler concentration could be associated with the blocking effect of the inorganic fillers in the conductivity pathway. The increase, for low filler concentration, could be, on the other hand, related to the reduction in the fusion enthalpy, which can be obtained by DSC measurement. Therefore, there is a maximum value of ionic conductivity with the optimized composition of composite ionic liquid gel polymer electrolytes.

Mechanical property of electrolytes Figure 2 shows the mechanical properties of these CILGPE by tensile tests. As shown in Fig. 2, the mechanical properties of these composite ILGPE were affected by the addition of inorganic particles. The addition of TiO₂ could increase their mechanical properties; the addition of Al₂O₃ and NiO would cause a poor mechanical property, while the concentration of CeO₂, SiO₂, Bi₂O₃, ZrO₃, and MgO would show the various effects on their mechanical properties, such as 15 wt% Bi₂O₃-ILGPE and 2.5 wt% display a poor mechanical property. By the mechanical properties and ionic conductivity measurements, we selected TiO₂ as a filler for the gel polymer electrolytes in this study.

Characterization of electrolytes According to the results of ionic conductivity measurements, we observe that the concentration of TiO₂ nanoparticles in the polymer matrix could affect ionic conductivity. As known to all, TiO₂ nanoparticles cannot conduct lithium-ions. Thereby, the addition of TiO₂ would sit in the lithium-ion pathway. The addition of high amounts of TiO₂ filler can reduce the ionic conductivity. The mechanism scheme is shown in Figure S1, indicating that the concentration of non-conductive fillers cannot be over the optimizing ratio. When the 5 wt% TiO₂ is added into ILGPE, the highest ionic conductivity is obtained and the value is 1.51 mS cm⁻¹.

To investigate the effects of TiO₂, the interaction between TiO₂, PP13TFSI, LiTFSI, and PVDF-HFP in composite gel polymer electrolytes was investigated by FT-IR and Raman spectroscopy (Fig. 3). By the FT-IR spectroscopy, the TiO₂ does not react with the PP13TFSI, LiTFSI, and PVDF-HFP during ILGPE preparation (Fig. 3a). In the ILGPE matrix, PP13TFSI, LiTFSI, and PVDF-HFP have

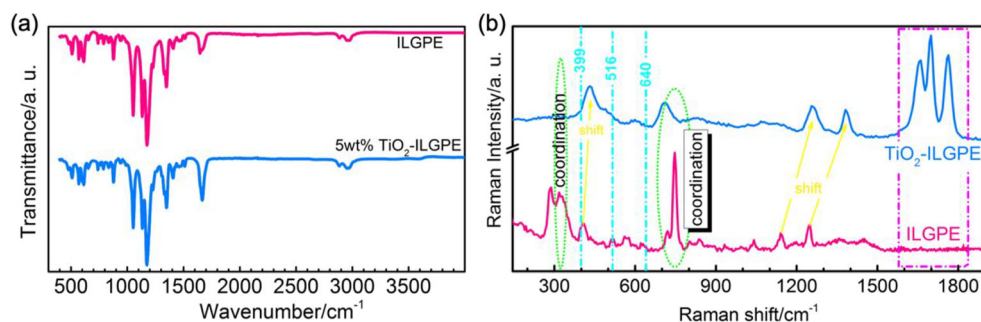
“coordination,” such as Raman shift of 315 cm⁻¹ and 740 cm⁻¹ (Fig. 3b). After the addition of TiO₂, however, these “coordination” disappeared or weakened, while the new “coordination” appeared around 1600–1800 cm⁻¹. The results indicate that TiO₂ could break the “original coordination” between PP13TFSI, LiTFSI, and PVDF-HFP, and then form a “new coordination” with PP13TFSI, LiTFSI, and PVDF-HFP. Thus, TiO₂ particles sit in the lithium-ion pathway and decrease lithium-ion transport [35].

Besides, the XRD pattern of 5 wt% TiO₂-ILGPE shows a new diffraction peak at 25° (2θ), indicating that the amorphous phase of PVDF-HFP increases by the 5 wt% TiO₂ (Figure S2). There is literature reporting that the amorphous phase of the polymer can increase the ionic conductivity of polymer electrolytes. That is the reason that the ionic conductivity increases and reaches the highest value and then decreases after that (5 wt%) [36–39].

Figure 4 shows the SEM images of the CILGPE with various weight percentages of TiO₂. ILGPE is a porous film and the pore size is less than 5 μm (as shown in Fig. 4a and a-magnified). With the addition of 5 wt% TiO₂, the pores of ILGPE are filled and the surface of CILGPE is getting smooth and flat (Fig. 4b), while with the weight percentage of TiO₂ increase, the surface of the CILGPE turns ununiform due to the TiO₂ particle aggregation (Fig. 4c). The compact surface of 5 wt% TiO₂ probably could inhibit lithium dendrites' growth and solve the safety issue of lithium metal batteries.

Safety of TiO₂-ILGPE We assembled a Cu/ILGPE/Li cell and a Cu/5 wt% TiO₂-ILGPE/Li cell, and then the lithium stripping/plating was carried out with a current density of 0.5 mA cm⁻² for long-term cycles. After the Cu/Li cells shorted, we disassemble them and the digital photos of ILGPE and 5 wt% TiO₂-ILGPE are shown in Figure S3. Figure S4 displays the pristine ILGPE and 5 wt% TiO₂-ILGPE before cycling, and these electrolytes are free-standing membranes. The color of the polymer electrolytes surface becomes “black” in some regions after cycling, because the deposited lithium metal adheres to the surface of the polymer electrolytes. The ILGPE membrane is still transparent, and the 5 wt% TiO₂-ILGPE membrane remains light yellow and nontransparent. The results indicate that TiO₂ is not reduced by lithium metal during

Fig. 3 FT-IR and Raman spectra of ILGPE and 5 wt% TiO₂-ILGPE in a range of 400–4000 cm⁻¹ and 150–2000 cm⁻¹, respectively



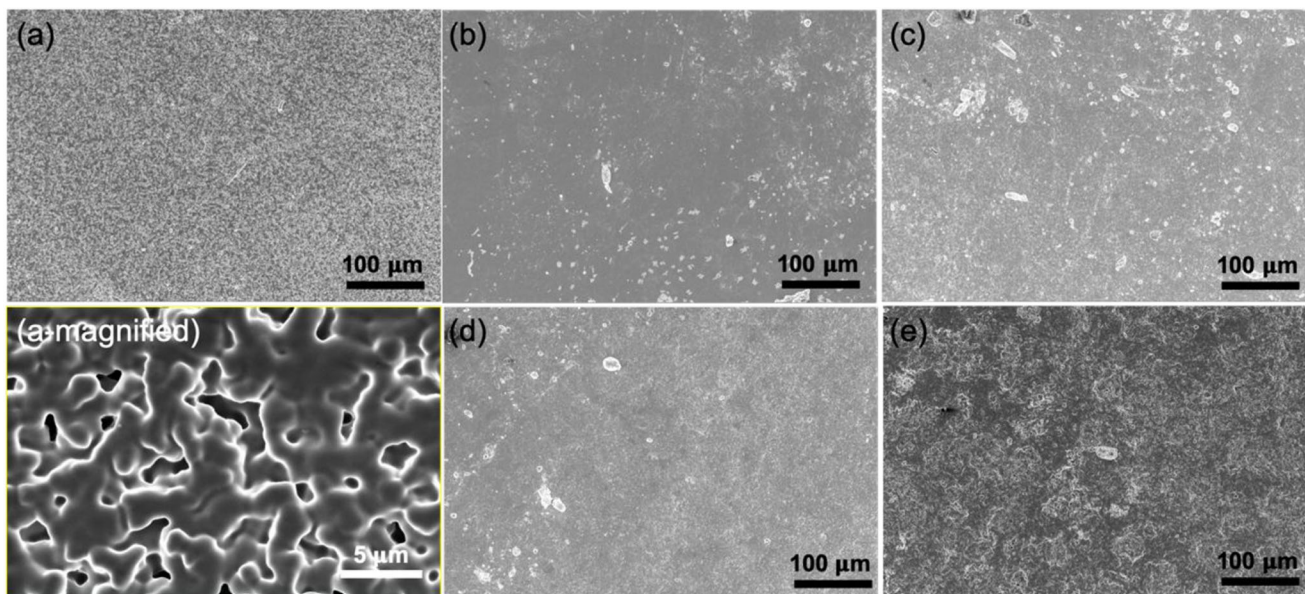


Fig. 4 SEM images of various weight percentage of TiO₂ composite ionic liquid gel polymer electrolytes. **a**, a-magnified ILGPE, **b** 5 wt% TiO₂-ILGPE, **c** 10 wt% TiO₂-ILGPE, **d** 15 wt% TiO₂-ILGPE, and **e** 20 wt% TiO₂-ILGPE

the charging/discharging. Meanwhile, we performed cycle voltammetry (CV) and battery measurements for the Li/5 wt% TiO₂-ILGPE battery with 1 M LiPF₆ EC/DMC (v/v = 1/1) as the electrolyte and glass fiber as the separator (Fig. 5). The CV curves do not show any redox peak, indicating that the Li/5 wt% TiO₂-ILGPE battery does not have any redox reaction in the measured voltage range (Fig. 5a). The cells cannot deliver a noticeable capacity during the constant current charging/discharging, indicating that TiO₂ particles in the ILGPE are not redox-active (Fig. 5b). In a word, TiO₂ fillers in the CILGPE do not reduce against lithium metal anode and its safety to add to polymer electrolytes.

The combustion test of the polymer electrolytes is performed, and the digital images are shown in Fig. 6. As shown in Fig. 6a, the PVDF-HFP membrane is flammable. When putting the PVDF-HFP membrane on fire, it shrinks immediately (~3 s) and gets on fire in a short time (~5 s). Finally, it turns “black” in color. The ILGPE is a non-flammable membrane, but it shrinks at ~5 s without blackening. While 5 wt% TiO₂-ILGPE is a non-flammable membrane, it displays a perfect flame retarding ability. Furthermore, both ILGPE and TiO₂-ILGPE are a promising electrolyte for safe lithium metal batteries.

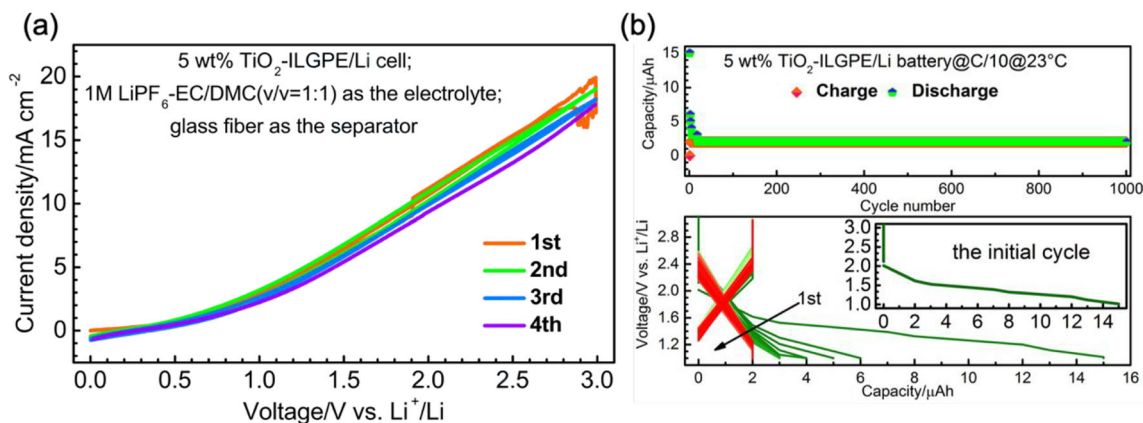


Fig. 5 **a** CV curves for the cell with 5 wt% TiO₂-ILGPE as the working electrode and Li-metal as the counter electrode (glass fiber as the separator, and 1 M LiPF₆ EC/DMC (v/v = 1/1) as the electrolyte) in a voltage range of 0–3 V (vs. Li⁺/Li) at a scan rate of 1 mV s⁻¹. **b** The voltage profile of Li/5 wt% TiO₂-ILGPE battery (5 wt% TiO₂-ILGPE as the

working electrode, Li-metal as the counter electrode and the reference electrode, glass fiber as the separator, and 1 M LiPF₆ EC/DMC (v/v = 1/1) as the electrolyte) at C/10 and 23 °C. The 1C is 335 mAh g⁻¹. The mass loading of the active material (TiO₂) of the working electrode is about 0.09 mg cm⁻²

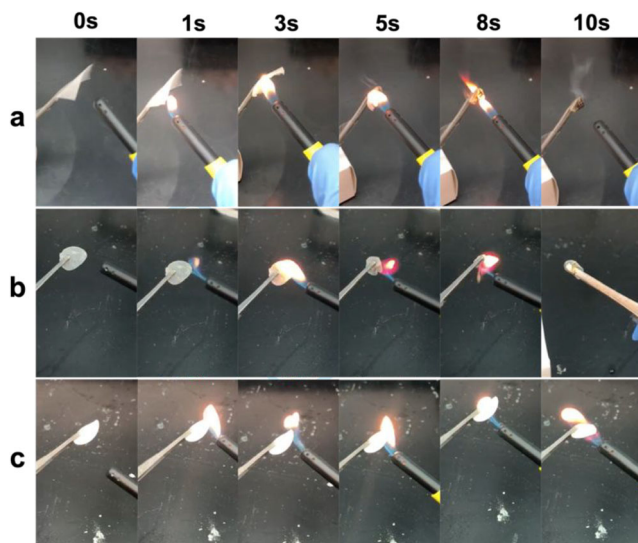


Fig. 6 Combustion test of (a) PVDF-HFP membrane, (b) ILGPE, and (c) 5 wt% TiO₂-ILGPE

Conclusion

In this study, the non-ionic conductive inorganic particles were used to improve the mechanical properties and ionic conductivity of gel polymer electrolytes. By the properties of these composite gel polymer electrolytes, TiO₂ particles were selected as the filler of gel polymer electrolytes. The addition of TiO₂ particles not only can fill the pores of gel polymer electrolytes to obtain dense electrolytes membrane but also can coordinate with the PP13TFSI or/and LiTFSI inside the composite gel polymer electrolytes. The safety of TiO₂-ILGPE was evaluated by cyclic voltammetry, battery performance, and combustion test. With TiO₂-ILGPE as an anode and Li-metal as a cathode, we assembled TiO₂-ILGPE/Li cells to investigate the stability of TiO₂-ILGPE against lithium metal. The results indicated that the TiO₂ particles would not undergo a redox reaction during TiO₂-ILGPE/Li cells cycling, and the cells delivered a charging specific capacity of 0.02 μAh g⁻¹ at C/10, which could be neglected. Besides, the TiO₂-ILGPE is a non-flammable membrane and a promising polymer electrolyte for the next generation of safe lithium metal batteries.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11581-020-03850-9>.

Authors' contributions P.Y., X.P., and Q.H. designed the experiments. X.P. and Q.H. performed preparation, materials characterization, and electrochemical measurements. L.L., J.Z., and M.A. participated in the scientific discussion. X.P. and Q.H. analyzed the data and wrote the manuscript with assistance from coauthors.

Funding The work was supported by the National Natural Science Foundation of China (Grant No. 21878061). X.P. and Q.H. acknowledge the support from China Scholarship Council.

Compliance with ethical standards

Conflict of interest The authors declare that there are no conflicts of interest.

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