Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

Nano-Zirconia Boosting Ionic Conductivity and Lithium Dendrite Inhibition Ability of Poly (1,3-dioxolane) Solid Electrolyte for High-voltage Solid-state Lithium Battery

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Experimental

1.1 Chemicals

DOL (containing about 75 ppm of butylated hydroxytoluene as inhibitor; 99.8%), LiTFSI (99.8%), and $LiPF_6$ (99.9%) were all purchased from Suzhou DuoDuo Chemical Technology Co., Ltd. PE separator (9μm thick) was purchased from Shenzhen Xuran Electronic Co., Ltd. Commercial 5% yttria stabilized zirconia (YSZ) was purchased from Shanghai China Metallurgical New Materials Co., Ltd.

1.2 Preparation and characterization of solid electrolyte

In this work, poly (1,3-dioxolane) (PDOL) solid polymer electrolyte was selected as the electrolyte polymer matrix. Commercial 5% yttria stabilized zirconia (YSZ) as filler. The preparation process is all carried out in a glove box: Firstly, 5 g 1,3-dioxolane (DOL), 0.1435 g lithium bis(trifluoromethylsulphonyl)imide (LiTFSI), 0.05g $LiPF_6$ and different amounts of YSZ fillers were mixed and stirred for 10 min. In order to investigate the effect of adding different contents of YSZ fillers on the properties of electrolytes in detail, we also tried to add 0, 0.005 g, 0.01 g, 0.015 g, 0.025 g, 0.05 g, 0.1 g, and 0.1 g commercialized YSZ into DOL, that is, 0%, 0.1%, 0.2%, 0.3%, 0.5%, 1.0% and 2.0% of YSZ fillers to DOL liquid mass. The specific membrane forming operations are as follows: First, 50% of the electrolyte solution is evenly coated on the glass plate with a scraper, then the polyethylene (PE) skeleton with the size of 100 mm × 70 mm × 9 μm is laid flat on the glass plate, and the remaining electrolyte solution is uniformly coated on the surface of the PE skeleton. Then the electrolyte solution polymerizes rapidly on the surface of the PE skeleton in about 20 minutes, and the PDOL-YSZ composite solid electrolyte membrane (CSEM) was prepared successfully. Then we hang the PDOL-YSZ CSEM to dry, after it was thoroughly dried, the PDOL-YSZ CSEM was cut into thin slices with a diameter of 19 mm by a slicer, and then stored in a glove box for cell assembly.

The dried PDOL-YSZ CSEM was sandwiched between two stainless steel electrodes (SS) to form SS/CSEM/SS block cells, or SS and Li plate to SS/CSEM/Li cell, or Li plate and Li plate to form Li/CSEM/Li symmetrical cells. The ionic conductivity of the electrolyte was calculated by measuring the impedance of the SS/CSEM/SS cell and through the formula $\sigma=L/(R\cdot S)$ (L is the thickness of the CSEM, R is the bulk resistance, and S is the contact area between the electrolyte membrane and the electrode). The electrochemical stable voltage of SS/CSEM/Li cell was measured by linear sweep voltammetry (LSV). The scanning rate was 0.2 mV/s between 0V to 7V (vs. Li^+/Li). Electrochemical impedance spectroscopy (EIS) was measured by Solartron 1287 multichannel potentiostatic electrochemical workstation with a bias voltage of 10 mV and a frequency range of 10MHz to 0.1Hz. The ion transfer number of Li/CSEM/Li cell was measured on an electrochemical workstation. The ion transfer number of solid electrolyte can be calculated by the formula $t_{Li}{}^{+}= [I_{SS} \times (V-I_0R_0)]/ [I_0 \times (V-IssRss)]$, (V is the applied voltage, I_0 and I_{SS} are the initial and stable currents, and R_0 and R_{SS} are the electrode/electrolyte interface resistance before and after polarization).

1.3 Preparation of solid electrodes

The traditional preparation method of aluminum foil-based electrode was adopted. The preparation process is all carried out in open air. It includes four steps:

slurry mixing, coating, drying and rolling. The cathode consists of 80% $LiCoO_2$(LCO) active substance, 12% conductive carbon black (Super-P), 4% polyvinylidene fluoride (PVDF), 4% chlorinated polyethylene (PEC), In addition, $LiClO_4$, which accounts for 10% of the total mass of PEC and PVDF was added. N-methyl pyrrolidone (NMP) is the solvent. The ratio of PVDF and PEC to NMP was 1:35. The collector is a commercial double-sided carbon-coated aluminum foil with a thickness of about 15 μm. The preparation process is as follows:

First, LCO and Super P were mixed and ground for 1 h, then dried at 100 ℃ for 10 h, PVDF and PEC powders were completely dissolved in NMP solution, and lithium salt $LiClO_4$ was added to NMP solution to stir 30min. Then, the mixture of LCO and Super P was added to the mixed NMP solution and stirred for 5 minutes with a defoaming agitator (2000 rpm for 3 min 30 s, 2200 rpm for 1 min 50 s). The defoaming process was carried out three times to obtain a uniform slurry. Then the paste is scraped on the collector at a scraping speed of 10, and the thickness of the coating on the aluminum foil is 125 μm. The prepared electrode is dried in a blast dryer at 60 ℃ for 8 hours, then vacuum dried at 100 ℃ for 12 hours, and then rolled repeatedly on a roller press until the thickness of the electrode plate remains unchanged. In this work, the aluminum foil electrode is rolled to ~30 um.

1.4 Cell assembly and test

The cells were assembled in an argon-filled glove box by sequentially stacking the cathode, CSEM membrane. In order to enhance the contact between electrolyte and electrode, 2.5 μL ester liquid electrolyte was added to each side of the CSEM for all cells, then sealed the cells with a cell sealing machine under the pressure of 50 kg/cm^2. The assembled cells were subjected to charge-discharge tests for the rate capability and cycle performance using a LAND system after standing for 12 h at room temperature, the range of charge/discharge voltage is 3.0 V~4.35 V, the specific capacity of 1C is 145 mAh/g. The impedance of the LCO/CSEM/Li cell was tested by Solartron1287 electrochemical workstation, and the test frequency range is 10^6-10^{-1}Hz. The ionic conductivity between PDOL+YSZ and DOL+LiTFSI liquid electrolyte at

20℃ to 80℃ was measured with a gradient of 10℃.All the above electrochemical performance tests were carried out at 25 ℃.

2. Other characterizations

Thermo Scientific K-Alpha+ was used to obtain the XPS spectra. The X-ray source was an Al Kα micro-focus monochromatic source. A Thermo Scientific Nicolet iS5 spectrometer was used to record the FT-IR spectrum of the material in attenuated total reflection mode. The liquid LiTFSI+ DOL, PDOL and PDOL+YSZ were dissolved in dimethyl sulfoxide-d6, and analyzed by ^{1}H NMR using Bruker 600M. The surface and cross-section morphology of the solid-state electrolyte membrane were characterized by Hitachi s4800 scanning electron microscope. NETZSCH STA 449F3 was used for thermogravimetric analysis of the CSEM, the temperature range was 20 to 600 ℃, and the heating rate was 5℃/min. LANDdt CT2001A/CT2001C was used to charge and discharge the battery. All tests are performed at 25 °C unless otherwise noted.

Results

Fig. S1 shows the good wettability between the PDOL-YSZ electrolyte solution and the PE skeleton. From the results, we can see that the PDOL electrolyte solution can be completely infiltrated on the PE skeleton in about 1min, and there is no problem of non-infiltration or poor wettability.

Time Electrolytes	0 s	30 s	60 s
0.3% YSZ			

Fig. S1 Contact angle measurement of the PDOL-0.3%YSZ solution and PE skeleton at different time.

Fig. S2 is the thermal stability of the PDOL-0.3%YSZ solid electrolyte which had been polymerized without coating film. After it was placed in the oven at 80 ℃ for 2 hours, the electrolyte remained solid, there was no flow and decomposition.

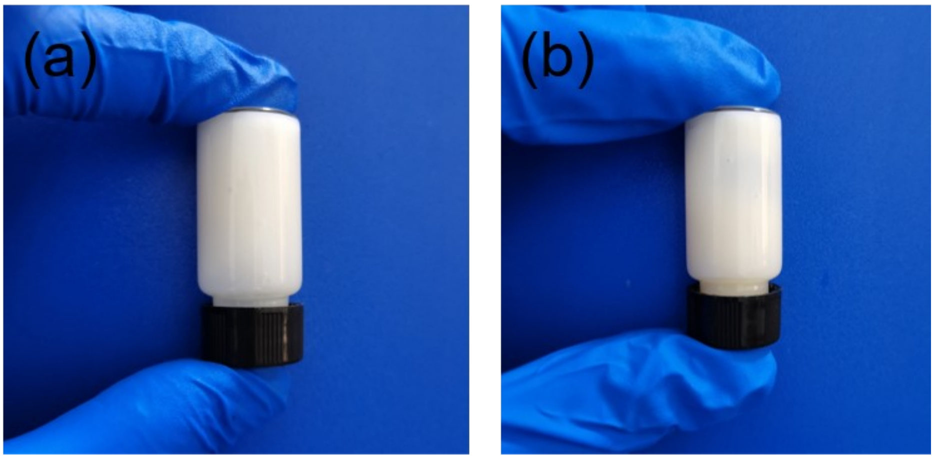

Fig. S2 Digital photos of PDOL-0.3%YSZ electrolytes (a) at room temperature and (b) heated at 80 ℃ for 2 hours.

Fig. S3 is the dependence of ionic conductivity on temperature. The results show that with the increase of temperature, the difference of ionic conductivity between PDOL+0.3%YSZ and DOL+LiTFSI liquid electrolyte decreases. In addition, the conductivity increases with the increase of temperature (T), showing a temperature dependence between room temperature and ionic conductivity. The linear shape of the graph shows typical Arrhenius type ($\sigma = A \exp(-E_a/kT)$) behavior. The linear relationship between 1000 T^{-1} and lgσ means that there is no obvious structural change in the electrolyte membrane within the test temperature range.

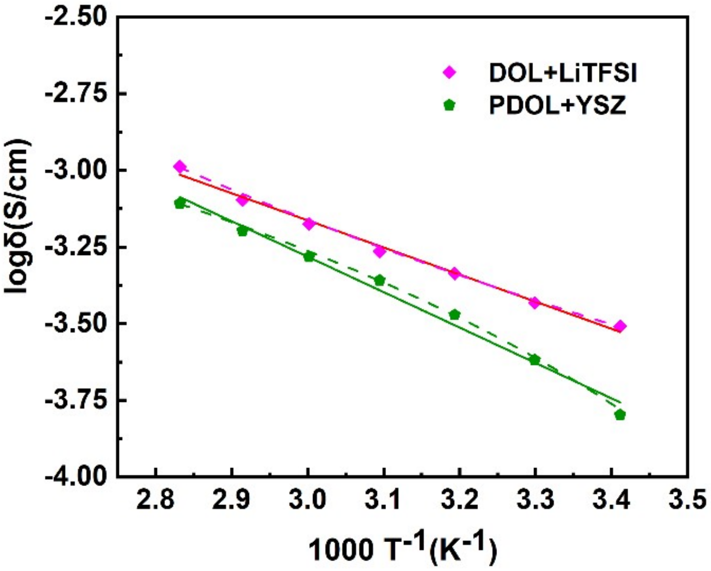

Fig. S3 Comparison of ionic conductivity between PDOL+0.3%YSZ and DOL+ LiTFSI liquid electrolyte, solid line and dashed line respectively represent the fitting data using Arrhenius transport model and Vogel-Fulcher-Tammann equation.

The LSV curves of full voltage range (0-7V) are shown in Fig. S4. The oxidation peak near 1.5V may be due to the intercalation, deposition and dissolution of Li^+ on steel sheet from lithium electrode, resulting in the generation of current. Then it remained stable until the voltage continued to increase and completely decomposed.

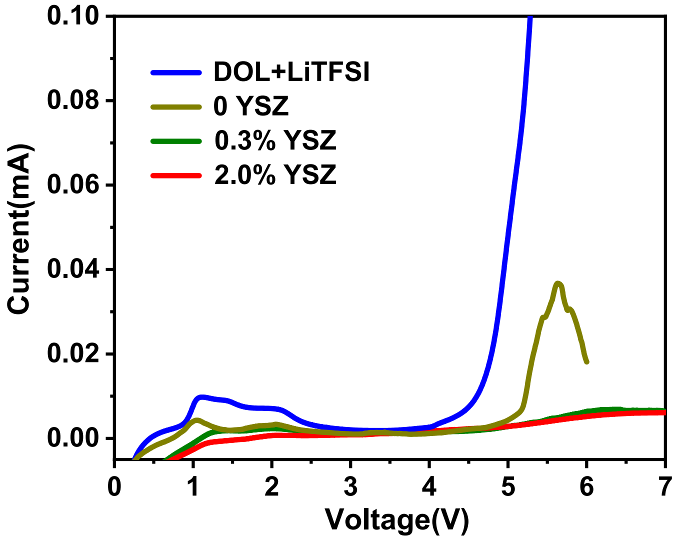

Fig. S4 Electrochemical stability windows in complete voltage range (0-7V) of CSEM with three additions and DOL+LiTFSI liquid electrolyte.

The surface SEM image of the recycled PDOL-0.3%YSZ CSEM is shown in Fig. S5. The result shows the surface of the membrane after cycling is still stable and intact, there are no serious cracks and holes.

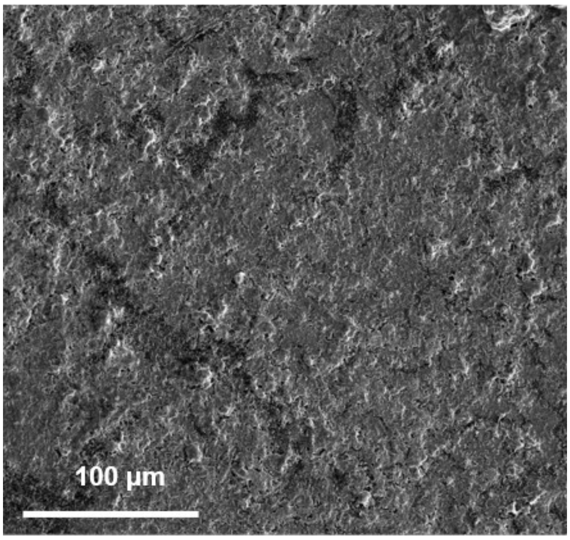

Fig. S5 SEM image of recycled PDOL-0.3%YSZ CSEM surface.

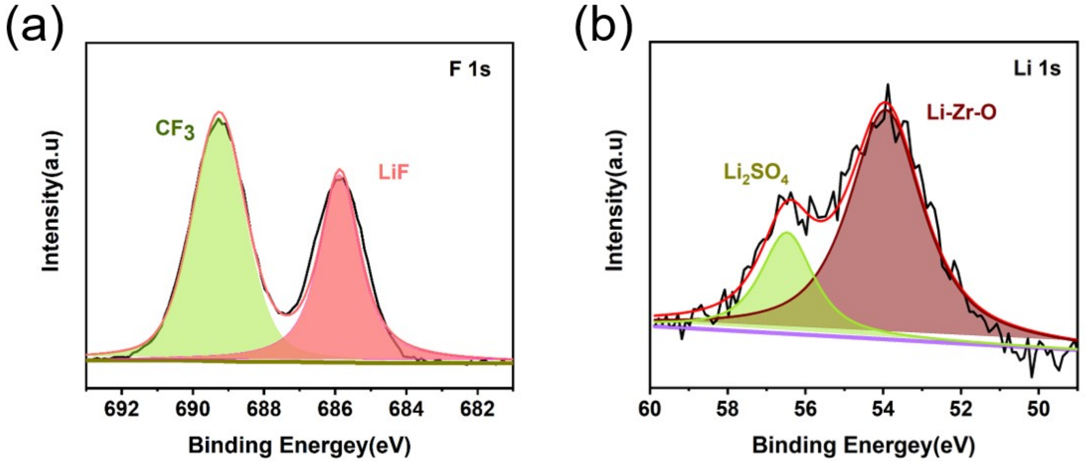

Fig. S6 XPS analyses for F 1s (a), Li 1s (b) performed on recycled PDOL-0.3%YSZ CSEM.

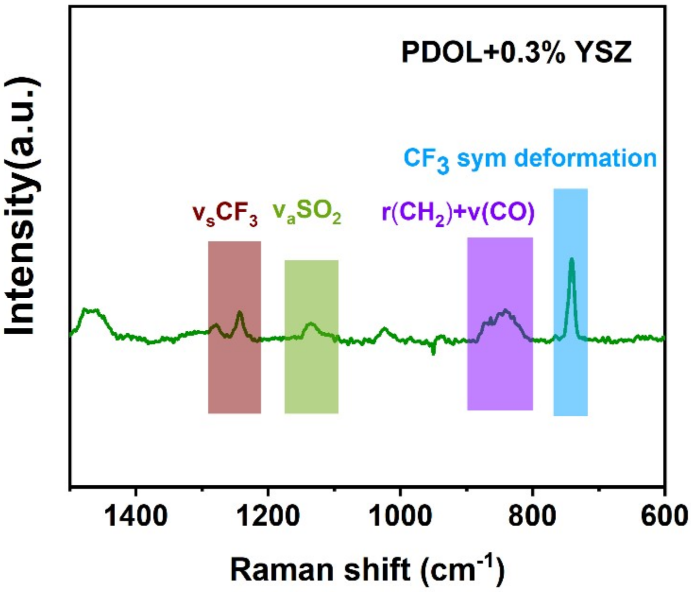

Fig. S7 Raman spectra of unrecycled PDOL-0.3%YSZ electrolyte.

Comparison with references

Table S1 lists the comparison of PDOL electrolytes and battery performances reported in the literatures. It shows that most of the current research on PDOL electrolyte is using in situ gelation method to produce gel-state electrolyte, which has poor mechanical properties, resulting in some restrictions on the inhibition of lithium dendrites and battery's safety improvement. In this work, we for the first time prepared PDOL-YSZ composite solid electrolyte membrane. The addition of commercial YSZ nanoparticles promotes the polymerization process of DOL and improves the physicochemical properties of electrolytes. Besides, YSZ can react with lithium anode to form stable solid electrolyte interface, which is beneficial to the interface stability between lithium anode. The membrane preparation method not only avoids the problems such as unstable process and uneven polymerization of commonly used in-situ polymerization, but also is closer to the existing battery production process and is easy to be practical.

Table S1 Comparison of the properties between references and this work.

No.	**Component and Status**	**Electrolyte performance**	**Battery performance**	**Safety**	**Cost and Process**	**Literature**
1	DOL+DME+LiPF$_6$+LiTFSI **In situ gel**	**1.Conductivity :** 5.50×10^{-4} S/cm **2. LSV:** 4.6V	**NCM$_{622}$ /PDOL/ Li cell** shows a initial discharge specific capacity of 160 mAh/g, and was cycled for 100 times at 0.5C.	1.GPE could help maintain a more stable SEI layer and higher reversibility of Li plating/stripping reaction. 2.GPE can partially restrain the shuttle effect and improve the safety performance of the battery. 3.The battery using GPE can still remain stable for more than 800 hours at 0.5 mA cm^{-2} without obvious voltage polarization variation.	Common experimental drugs, the experimental conditions are relatively common, no heating and other operations. **In situ gel method**	F.-Q. Liu, et al, *Science Advances*, 2018, 4, eaat5383.
2	DOL+Al(OTf)$_3$+LiTFSI **In situ gel or solid**	**1.Conductivity :** 1.8×10^{-3} S/cm at gel; ~10^{-4} S/cm at solid **2. LSV:** 4.8~5.0V	**LiFePO$_4$ /PDOL / Li shows a** initial discharge specific capacity of 130 mAh/g, and was cycled for 200 times at 0.2C with the retention capacity of 100 mAh/g.	1.SPE cells can operate stably beyond 200 cycles at 1 mA cm^{-2}. 2.Substantial thin SEI formed on the surface of the metal Li using poly-DOL SPEs.	Common experimental drugs, the experimental conditions are relatively common, no heating and other operations. **In situ polymerization method**	Q. Zhao, et al, *Nature Energy*, 2019, 4, 365-373.
3	DOL+LiDFOB+LiTFSI **In situ gel**	**1.Conductivity :** 3.9×10^{-4} S/cm **2. LSV:** ~5.1V	**LiCoO$_2$/ PDOL/ pretreated-Li** After 60 cycles at 0.1C at 40 °C, the discharge specific capacity is reduced from about 140 mAh/g to about 80 mAh/g.	1.Cell with pretreated-Li anode and GPE performs a highly stable cycling at 0.5 mA cm^{-2} for 700 h. in-situ-formed. 2.GPE and constructed artificial SEI on Li anode is essential to regulate a stable interface toward Li anode.	Common experimental drugs, the precursor should be heated to 60 ºC for 12 hours. **In situ gel method**	Q. Liu, et al, *Journal of Materials Chemistry A*, 2020, **8**, 7197-7204.
4	DOL+LiFSI **In situ gel**	**1.Conductivity :** 7.9×10^{-3} S/cm **2. LSV:** ~5V	**LiFePO$_4$/PDOL/ Li** After 500 cycles at 1.0C, the discharge specific capacity is reduced from about 145 mAh/g to about 100 mAh/g.	1.The overpotential increases to 42 mV after the 1089th cycle. 2. SPE can inhibit the growth of lithium dendrites.	Common experimental drugs, the experimental conditions are relatively common, no heating and other operations. **In situ gel method**	H. Cheng, et al *Materials Today Energy*, 2021, **20**.
5	DOL+LiPF$_6$+LiTFSI **Solid film**	**1.Conductivity :** 2 ×10^{-4} S/cm **2.LSV:** 5V	**NCM622/PDOL/Li** The initial discharge specific capacity is about 152 mAh/g, and the capacity retention up to 100 mAh/g after 900 cycles at 0.5 C.	1.The PDOL electrolyte membrane is stable for more than 1500 h at 0.3 mA/cm^2, the overpotential rises only slightly. 2.PDOL electrolyte membrane can transport lithium ions rapidly and evenly, significantly delay the growth of lithium dendrites, and has high electrochemical stability.	Common experimental drugs, the experimental conditions are relatively common, no heating and other operations. **Scraping and coating method, close to the existing battery production process**	H. Yang, et al, *Chemical Engineering Journal*, 2021, **421**.
6	DOL+LiPF6+LiTFSI+YSZ fillers **Solid film**	**1.Conductivity :** 5.82×10^{-4} S/cm **2.LSV:** 5.1V	**LiCoO$_2$/PDOL-YSZ/Li** The initial discharge specific capacity is about 160 mAh/g, and the retention up to 96.1% after 200 cycles at 0.5C.	1.The CSEM can cycle stably for nearly 1500 hours at 0.5 mA cm^{-2}. 2.Li-Zr-O composite layer is formed on the lithium metal surface, which is beneficial to inhibit the growth of lithium dendrite.	Except the experimental chemicals, there is no extra cost, and the experimental conditions are relatively common, no heating and other operations. **Scraping and coating method, close to the existing battery production process**	This work