

**Ion-conductive vs. non-ion-conductive ceramic fillers  
in silane-linked polyethylene oxide-based composite polymer electrolytes  
with high room-temperature ionic conductivity**

**Electronic Supplementary Information**

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**Electrochemical measurements:**

Chronoamperometry and EIS were conducted to calculate the Li ion transference number ( $T_{Li}$ ) of the CPEs with the potentiostat (VSP-300, Biologic, France). Li | CPE | Li symmetric cells were assembled and placed in the climate chamber at 40 °C. The  $T_{Li}$  of CPEs were calculated with the following Equation A1.

$$T_{Li} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \quad (\text{A1})$$

The potential polarization voltage of  $\Delta V$  10 mV was applied.  $R_0$  and  $R_s$  are the initial and steady-state resistances of the cells, respectively.  $I_0$  and  $I_s$  are the initial and steady-state current values.

Linear sweep voltammetry (LSV) tests were carried out to evaluate the electrochemical stability window of the Li | CPE | Copper foil cells with the potentiostat and 10 mV s<sup>-1</sup> was applied from 0 V – 8 V at 40 °C. Lithium plating stripping tests were performed at a current density of 0.1 mA cm<sup>-2</sup> at 40 °C.



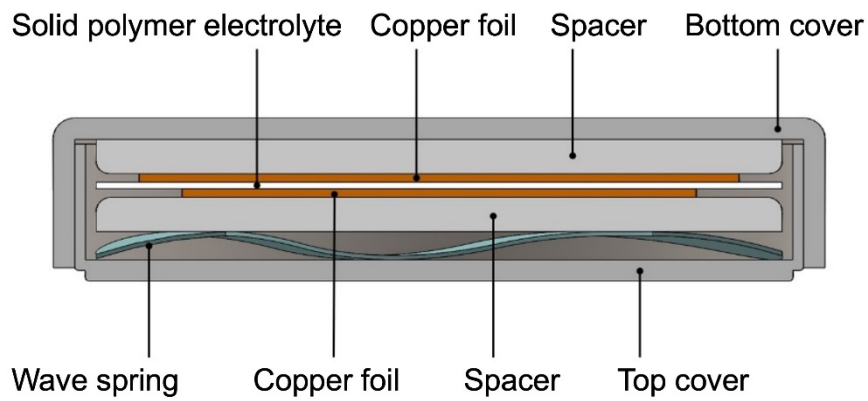
**Table S1.** Characteristics of functionalized passive filler-containing PEO-based CPEs from the literature

Polymer and salt	Filler and filler content in the CPE	Silane agent and its content in functionalized LLZO	Ionic conductivity	$E_a$	$T_{Li}$	Cycling performance
<sup>1</sup> PEO-LiTFSI (EO:Li 20:1)	ZrO <sub>2</sub> (vertical channels)	Ionic liquid ([PY1,3][TFSI])	$1.41 \times 10^{-4}$ S cm <sup>-1</sup> at 60 °C	0.16 eV	0.48	Initial discharge capacity: 135 mAh g <sup>-1</sup> at 2 C at 60 °C  LFP/CPE/Li metal
<sup>2</sup> PEO-LiTFSI (EO:Li 18:1)	3 wt.% of TiO <sub>2</sub> nanofibers	Polydopamine	$4.36 \times 10^{-4}$ S cm <sup>-1</sup> at 55 °C	-	0.190	Initial discharge capacity: 153.83 mAh g <sup>-1</sup> at 0.5 C at 25 °C  LFP/CPE/Li metal
<sup>3</sup> PEO-PPO-EMIM-TFSI	0.1 wt.% of SiO <sub>2</sub>	Triethoxysilane	$2.22 \times 10^{-3}$ S cm <sup>-1</sup> at 25 °C	-	-	-

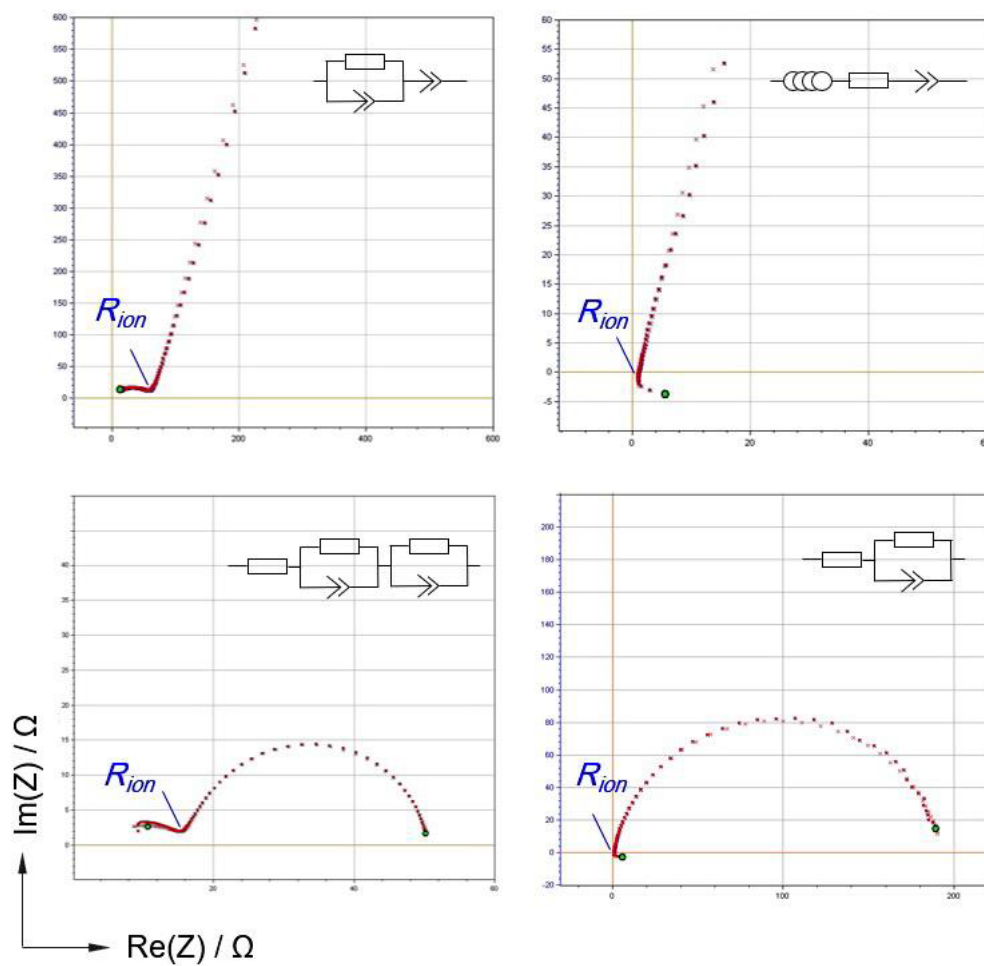
<sup>1</sup> Liang, Y., Chen, N., Qu, W., Yang, C., Li, L., W. Feng., Chen, R. (2021) Vertical Channels Design for Polymer Electrolyte to Enhance Mechanical Strength and Ion Conductivity. ACS Appl. Mater. Interfaces 2021, 13, 36, 42957–42965 (doi: 10.1021/acsami.1c13834)

<sup>2</sup> Zhao, E., Guo, Y., Zhang, A., Wang, H., Xu, Guangri. (2021). Polydopamine coated TiO<sub>2</sub> nanofiber fillers for polyethylene oxide hybrid electrolytes for efficient and durable all solid state lithium ion batteries. Nanoscale, 14, 890-897 (doi: 10.1039/D1NR06636F)

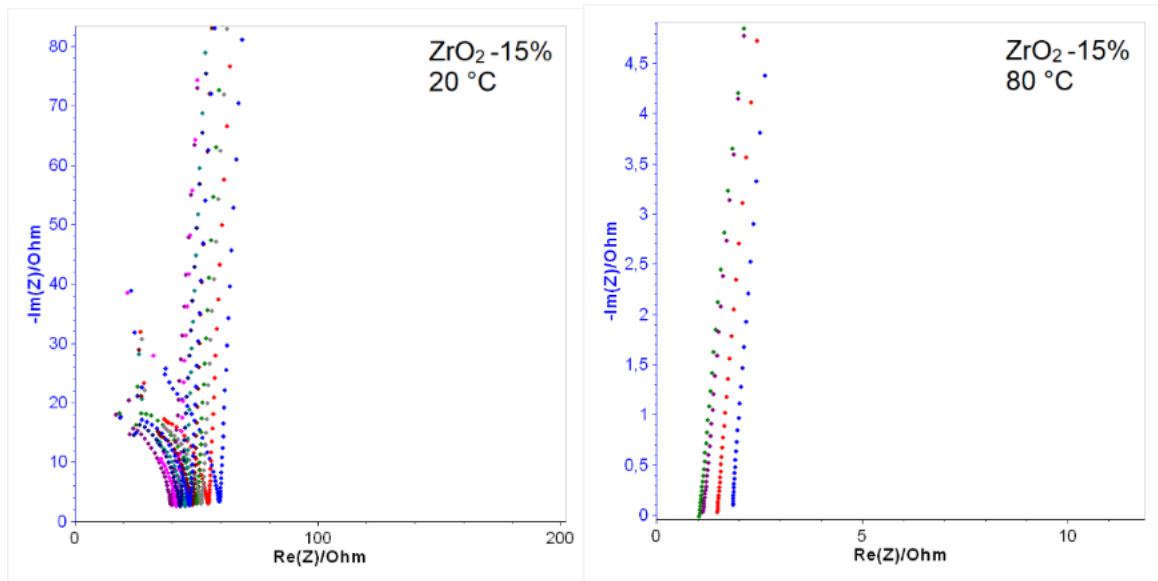
<sup>3</sup> Kim, S., Han, J. H., Lee, J. Y., So, S., Yoon, S. J., Kim, H-J., L, K. T., Kim, T-H. (2021). Cross-Linked Composite Gel Polymer Electrolyte Based on an H-Shaped Poly(ethylene oxide)–Poly(propylene oxide) Tetrablock Copolymer with SiO<sub>2</sub> Nanoparticles for Solid-State Supercapacitor Applications. ACS Omega, 6, ,26, 16924-16933 (doi: 10.1021/acsomega.1c01623)



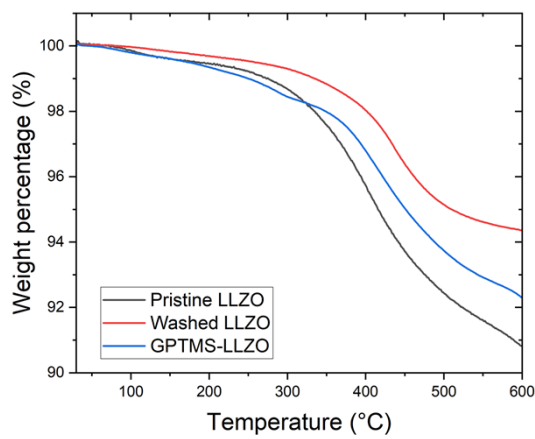
**Figure S1.** Schematic illustration of the cell components for EIS measurement



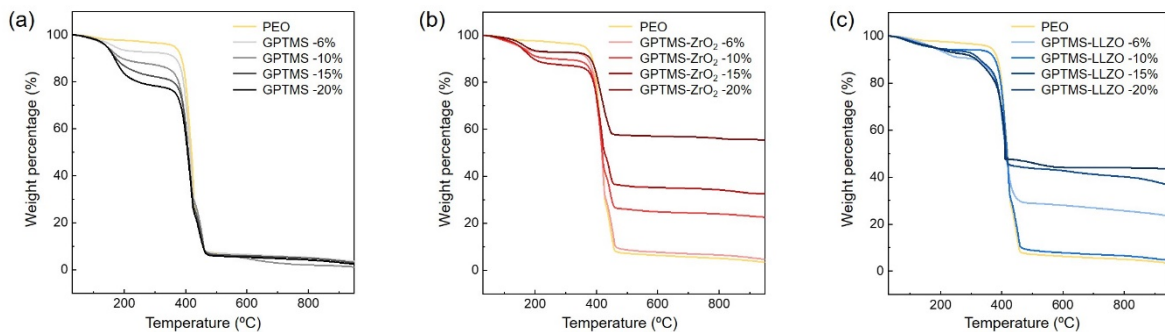
**Figure S2.** Fitting models for the EIS spectra with the corresponding equivalent circuit models



**Figure S3.** Examples of Nyquist plots of GPTMS-ZrO<sub>2</sub> -15% CPE cells at 20 °C and 80 °C

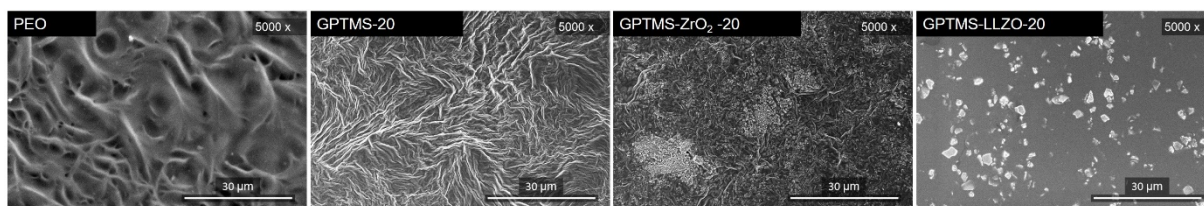


**Figure S4.** TGA thermograms of pristine, washed, and GPTMS-LLZO particles.



**Figure S5.** TGA thermograms of the CPEs.

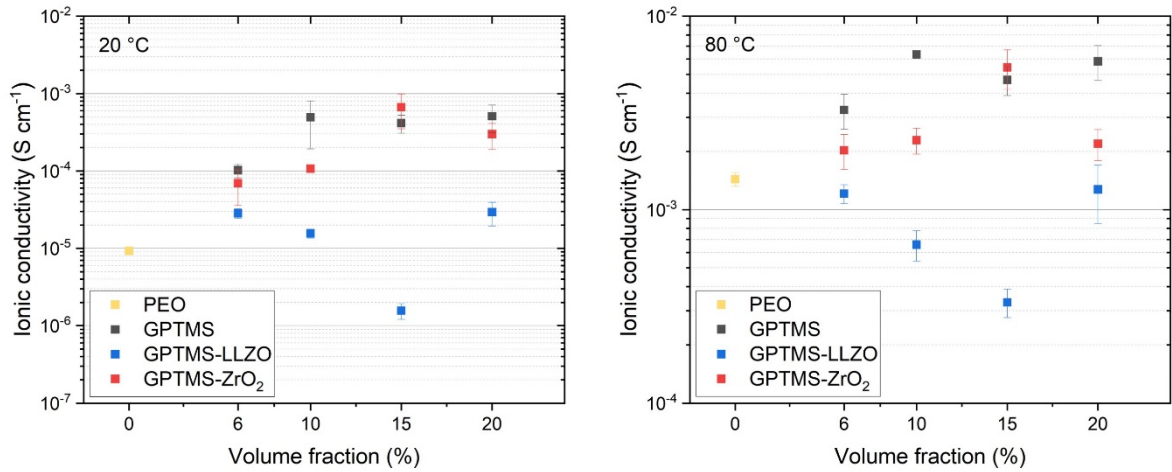
The TGA thermograms of the GPTMS CPEs (6, 10, 15, and 20 vol.%) and the PEO-LiTFSI SPE have a difference in thermal behavior especially in the range of 100 to 350 °C due to the decomposition of Si-R groups above 100 °C<sup>4</sup>. The resulting weight loss in each GPTMS CPEs occurs in proportion to the amount of GPTMS present in their composition. For example, at 300°C, the weight of the PEO solid electrolyte remains at 96.62%, while the weight of the GPTMS -6% CPE remains at 92.47% (GPTMS -10%, 15%, and 20% have 87.23%, 82.22%, and 78.27, respectively.). The organic components begin to decompose at a temperature of 300 °C and show significant mass loss at 400 °C. A decrease is also observed at 400 °C, which is attributed to the decomposition of LiTFSI<sup>5</sup>. The mass is relatively stable from 500°C to 950°C for all CPEs until it reaches a mass in the range of 1.2% to 3.4%. The filler containing CPEs had similar thermal behavior, as the weight loss is proportional to the amount of fillers in the composition. In general, it can be concluded from the comparison of the TGA spectra of the CPEs had an improved influence on the thermal stability, especially at the higher volume fractions 20% and 15%.



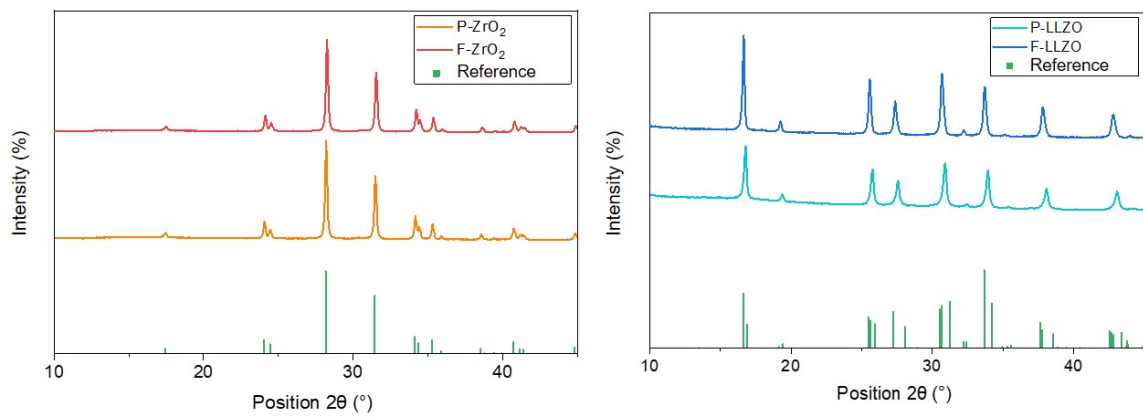
**Figure S6.** SEM images of PEO SPE, PEO-PEG-LiTFSI-GPTMS 20% CPE, PEO-PEG-LiTFSI-GPTMS-ZrO<sub>2</sub> 20% CPE, and PEO-PEG-LiTFSI-GPTMS-LLZO 20% CPE

<sup>4</sup> Embarek, N., Sahli, N. (2020). A Novel Green Synthesis Method of Poly (3-Glycidoxypropyltrimethoxysilane) Catalyzed by Treated Bentonite. *Bulletin of Chemical Reaction Engineering & Catalysis*, 15 (2), 290-303 (doi:10.9767/bcrec.15.2.6568.290-303)

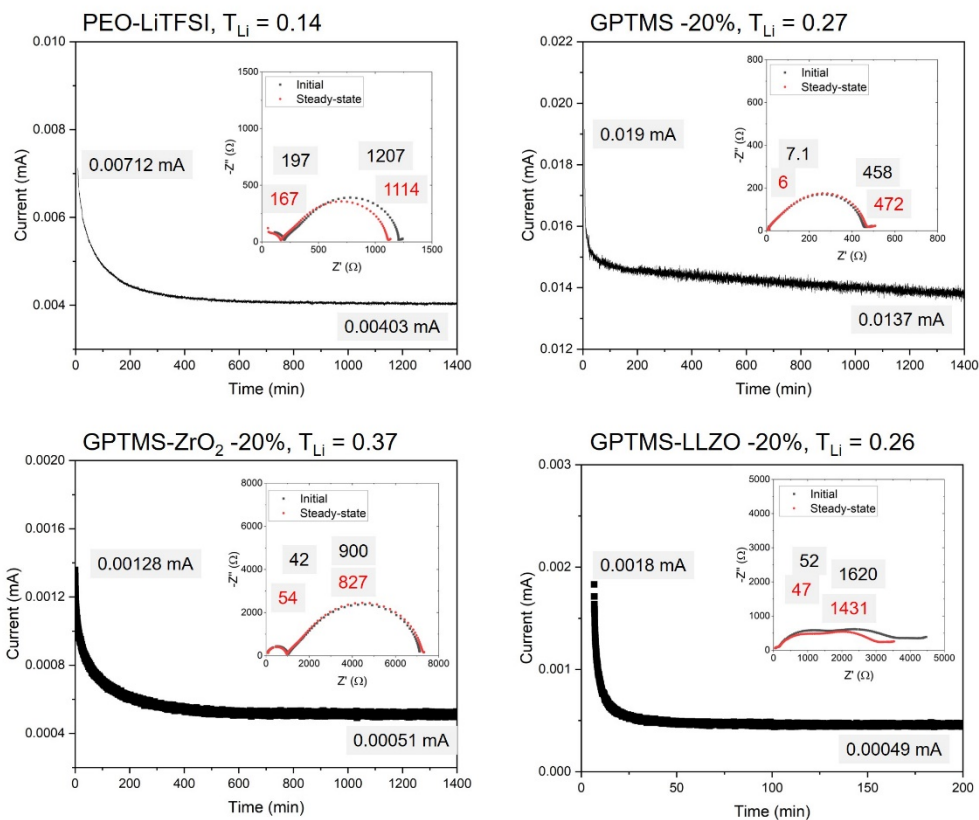
<sup>5</sup> Coeler, M.; van Laack, V.; Langer, F.; Potthoff, A.; Höhn, S.; Reuber, S.; Koscheck, K.; Wolter, M. Infiltrated and Isostatic Laminated NCM and LTO Electrodes with Plastic Crystal Electrolyte Based on Succinonitrile for Lithium-Ion Solid State Batteries. *Batteries* 2021, 7, 11. (doi.org/10.3390/batteries7010011)



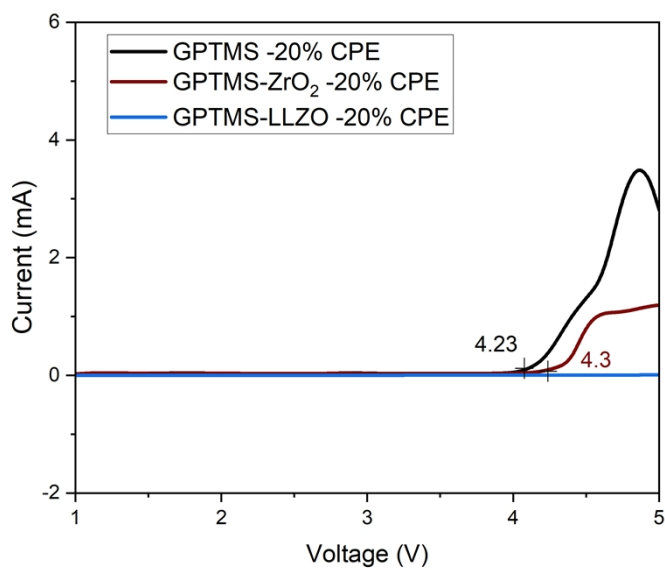
**Figure S7.** Direct comparison of PEO, GPTMS, GPTMS-LLZO, GPTMS-ZrO<sub>2</sub> CPEs as a function of volume fraction of GPTMS, GPTMS-LLZO, and GPTMS-ZrO<sub>2</sub> at 20 °C and 80 °C



**Figure S8.** XRD results of ZrO<sub>2</sub> and LLZO particles before and after functionalization



**Figure S9.** Chronoamperometry curves of the Li | CPE | Li cells recorded with a potential step of 10 mV at 40 °C and the inset graphs are the impedance spectra of the cells before and after polarization.



**Figure S10.** LSV curves of the Li | CPE | Copper foil cells at 40 °C.