Supplementary Information for

Engineered Interfaces in Hybrid Ceramic-Polymer Electrolytes for use in All-Solid-State Li Batteries

Parameswara Rao Chinnam and Stephanie L. Wunder

Department of Chemistry, Temple University, Philadelphia, PA 19122, USA

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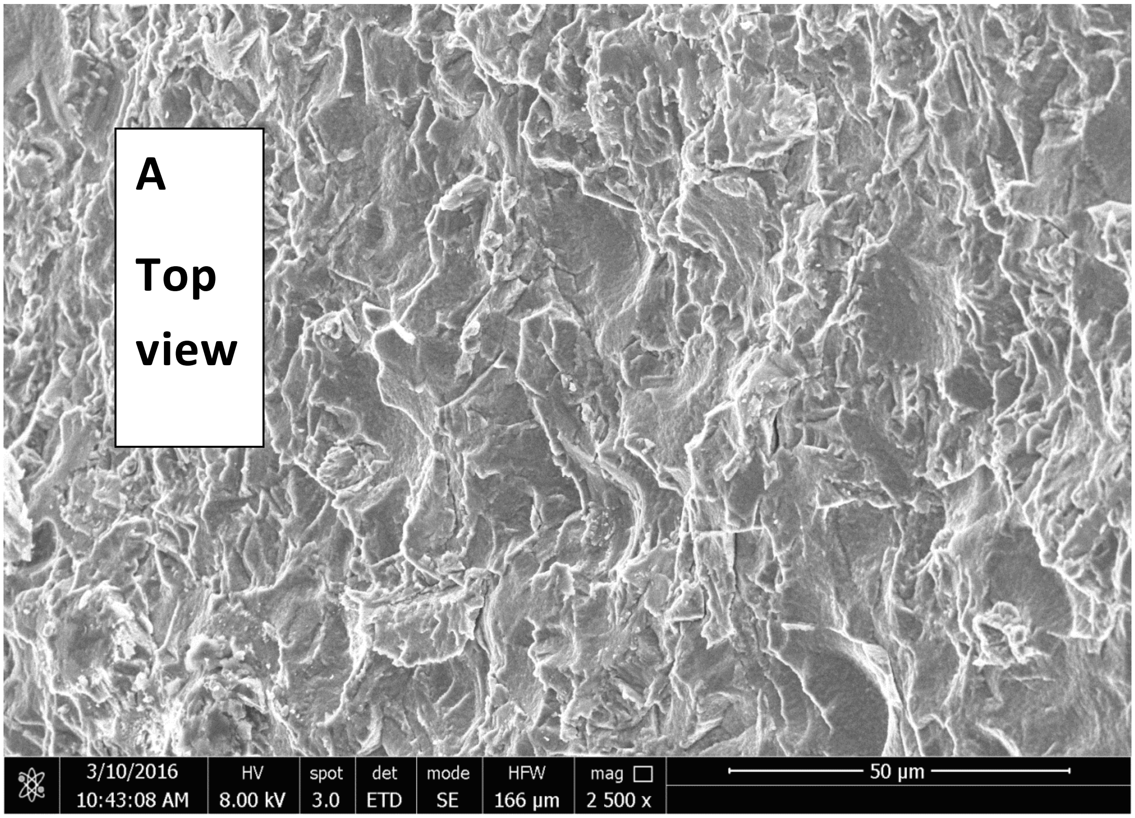
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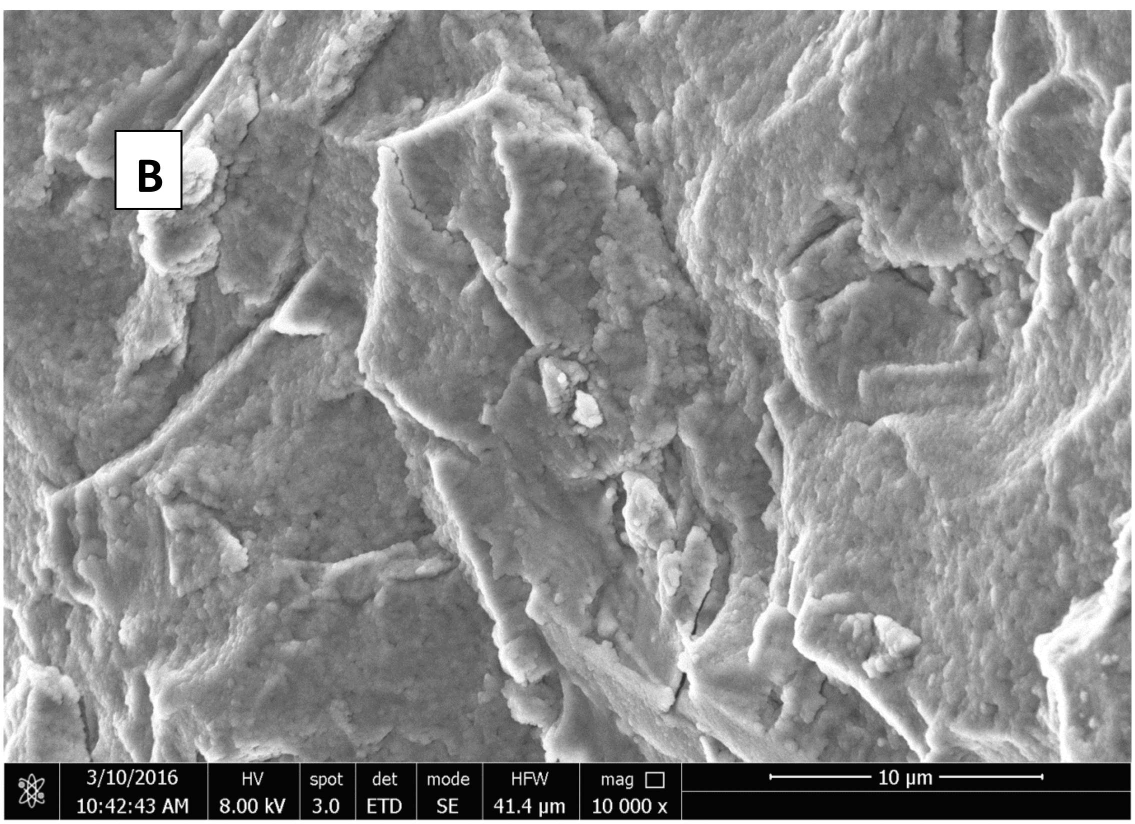
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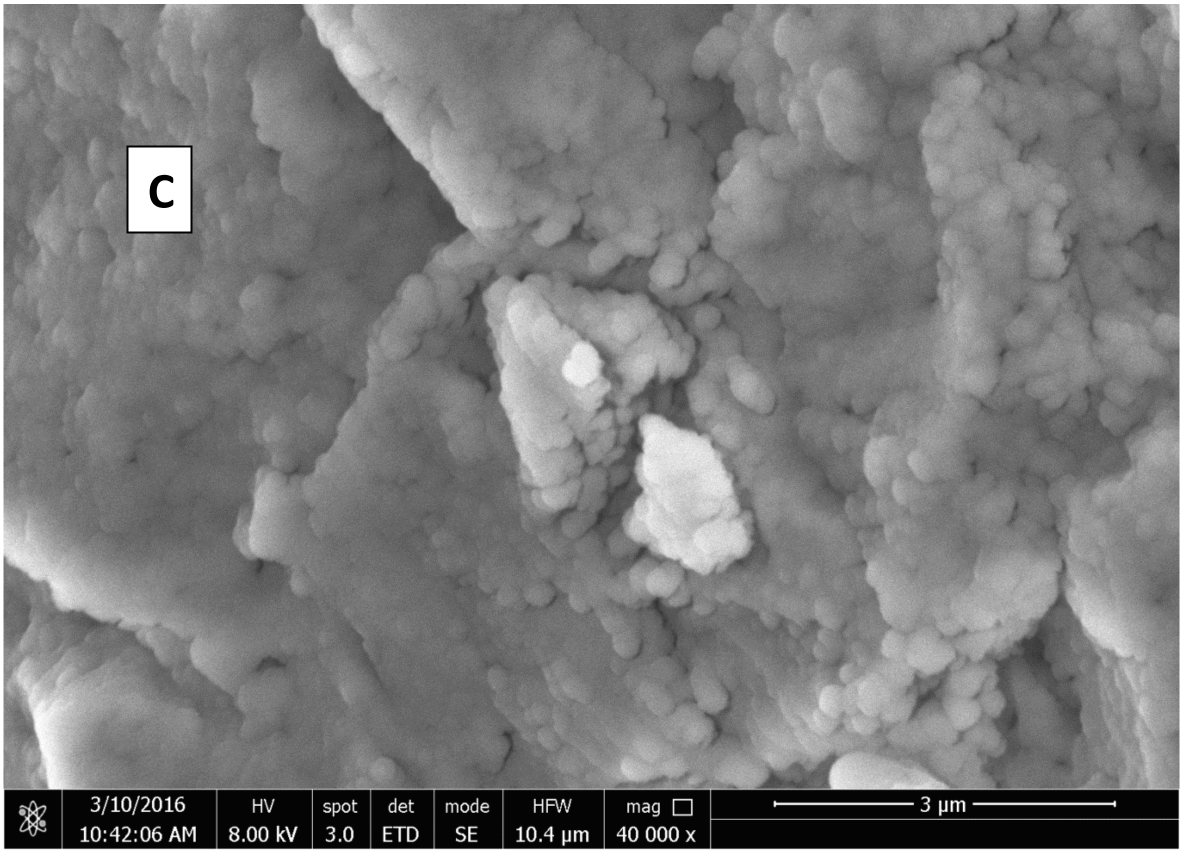
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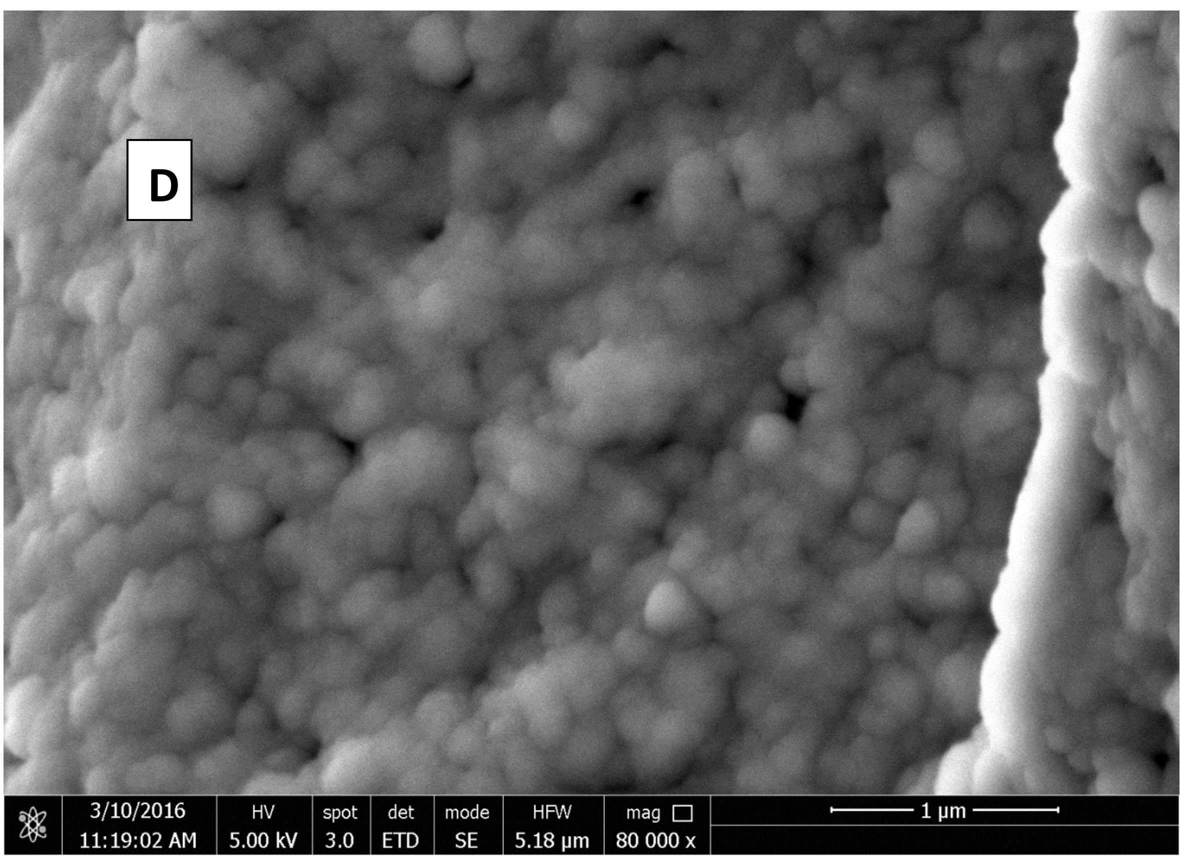
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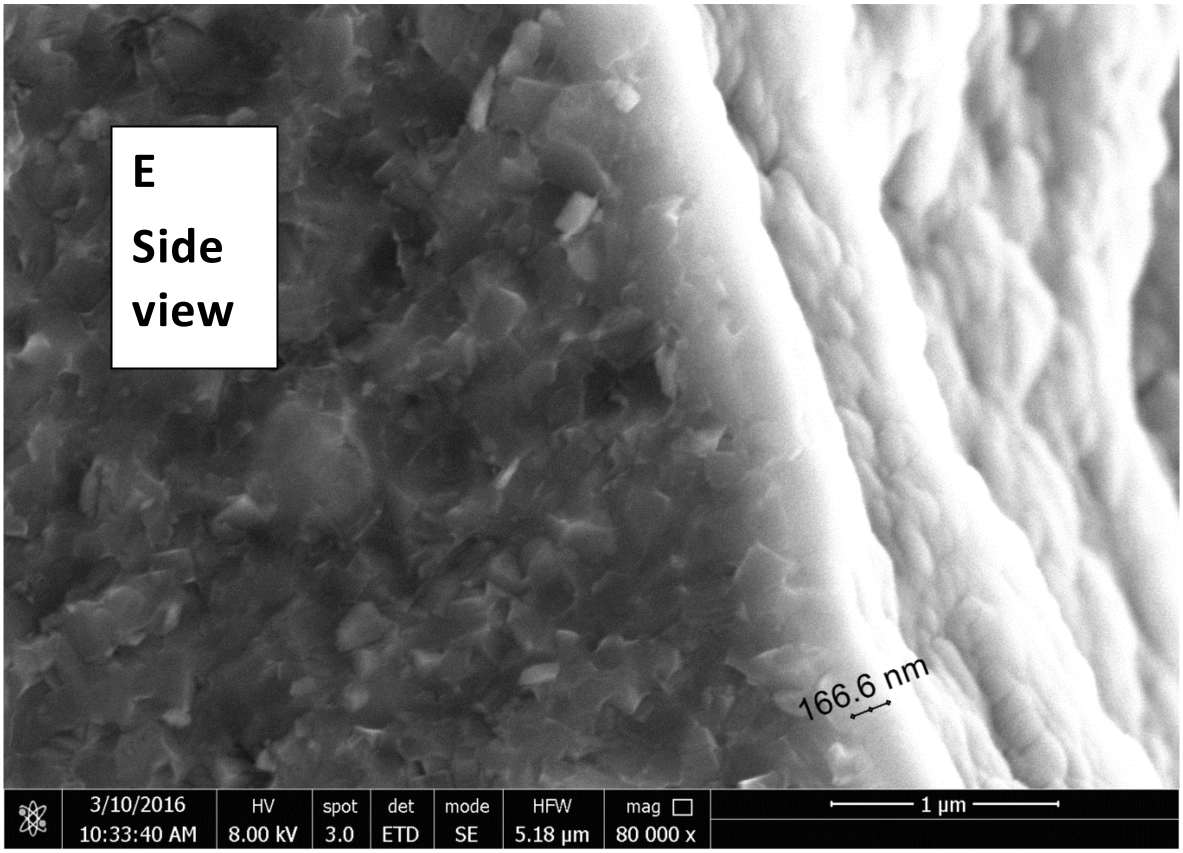


Figure S1. SEM images of SiO_2-LICGC at different magnifications: (**A-D**) top views; (**E**) side view showing LICGC and 166 nm conformal SiO_2 coating

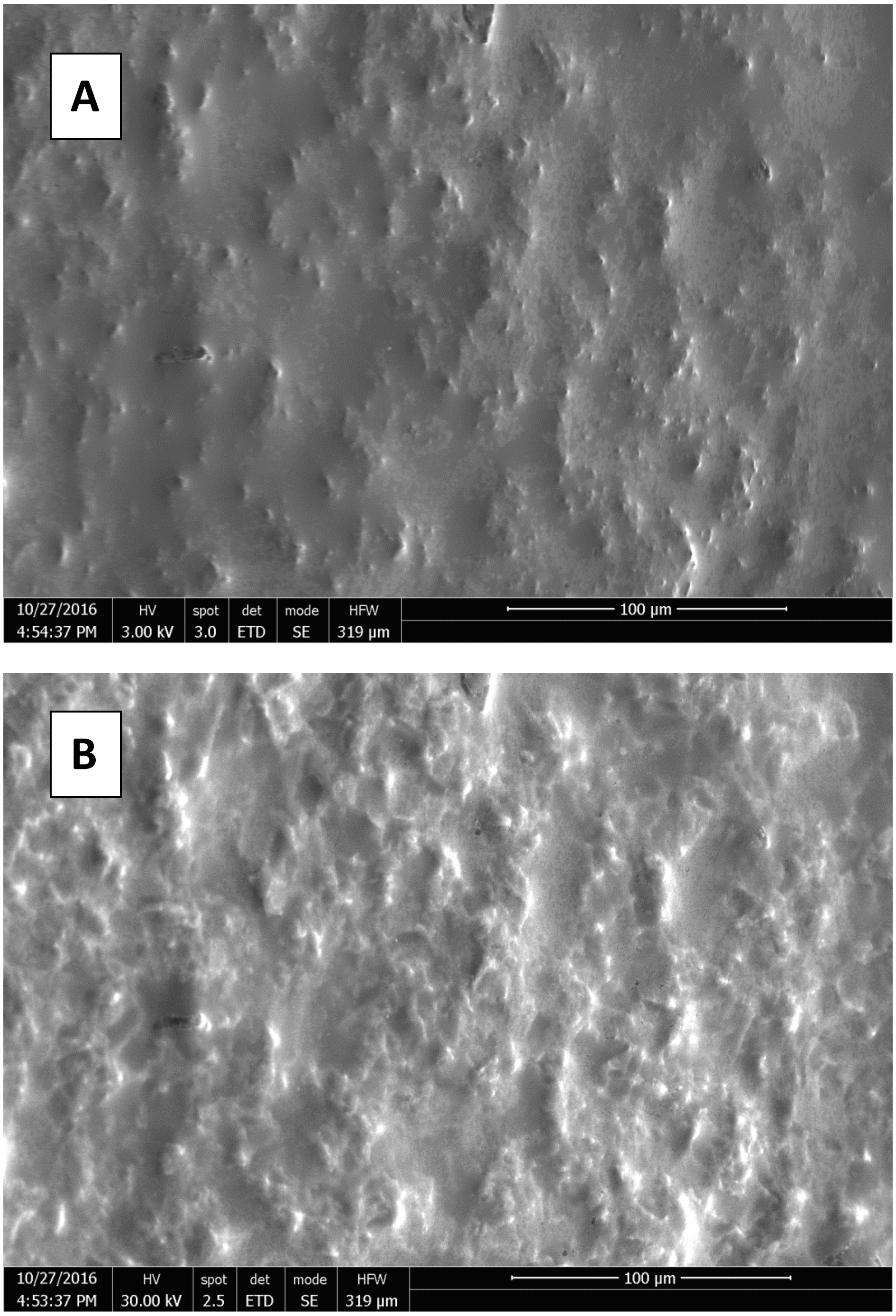


Figure S2. SEM images of SiO_2-LICGC silanated with PEG-silane/LiTFSI (O/Li = 12/1): (**A**) at 30 KV; (**B**) at 3KV. Secondary electrons are generated at the surface of the sample and provide topographic information. A high accelerating voltage results in most of the primary electrons traveling deeper into the sample and provides information about the sub-surface. Here 30KV was used to see the morphology of the ceramic surface underneath the silanated and crosslinked PEG-silane (**A**). When a low accelerating voltage is applied, it provides surface information with better resolution, especially for low density samples such as polymers. Here we used 3KV to see the silanated ceramic surface (**B**). From a comparison of **A and B**, it is clear that the surface of LiCGC-SiO_2 is covered with the crosslinked silanated PEG/$LiClO_4$.

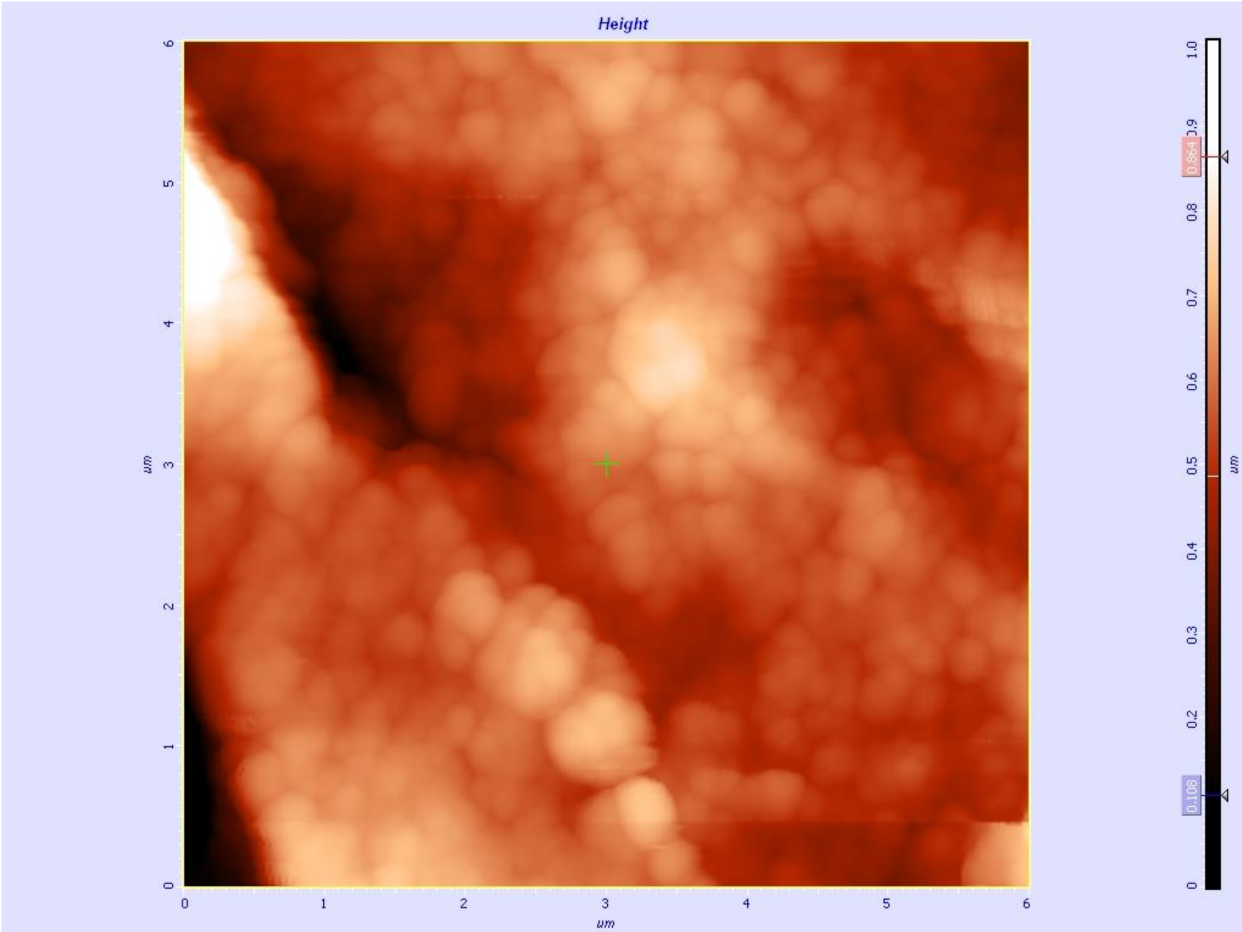


Figure S3. AFM image of SiO_2-LICGC top view

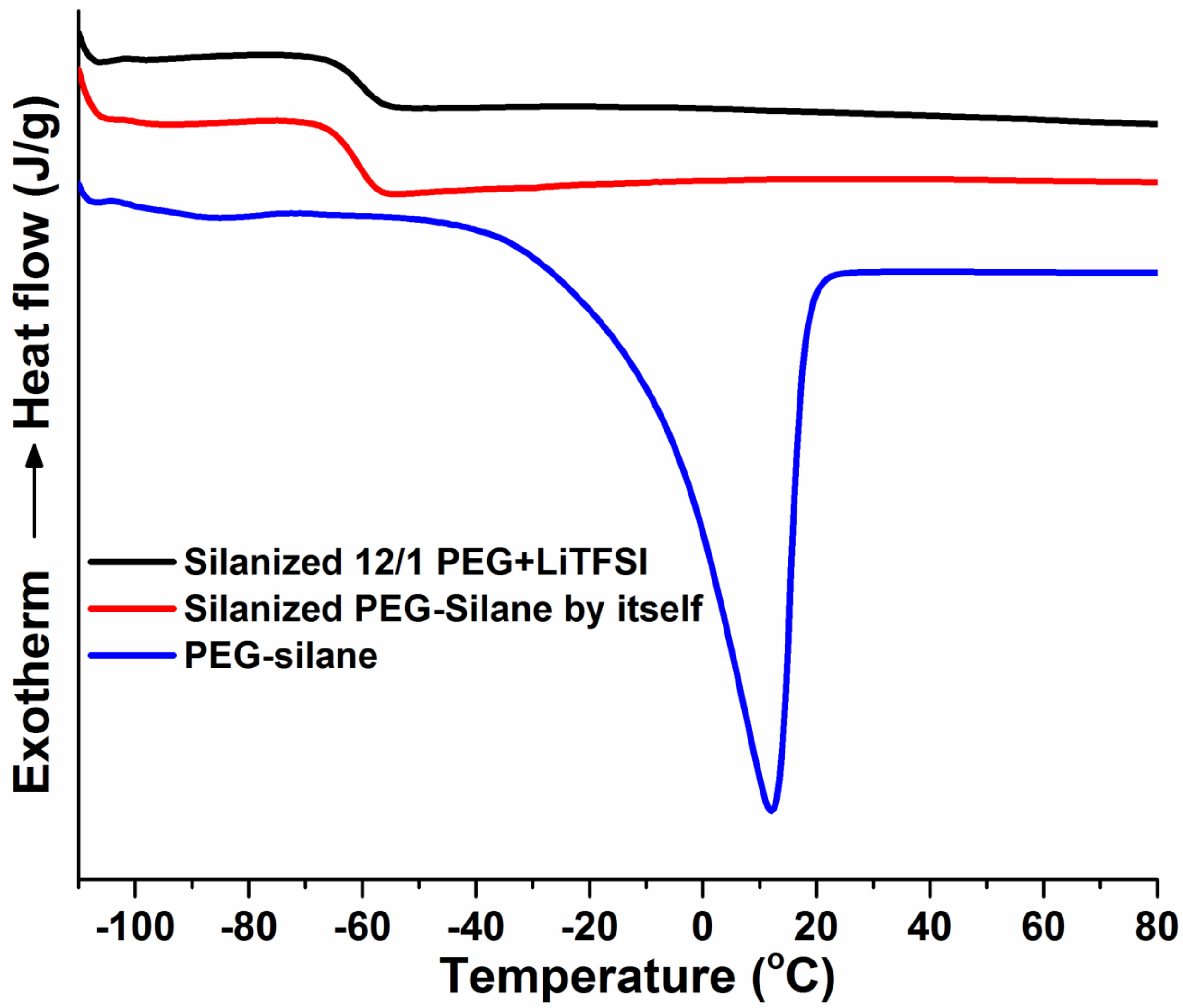


Figure S4. DSC data of PEG-silane (—), crosslinked PEG-silane (—) and PEG-silane crosslinked in the presence of LiTFSI (O/Li) = 12/1 (—). This demonstrates that all of the PEG-silane is bonded/crosslinked with the SiO_2 and that there is no free PEG-silane in the SiO_2 interface.

EIS data for pure LICGC

EIS data were obtained for pure LICGC between stainless steel (SS) electrodes using conductive carbon paste for good contact. At low temperature there are two distinguishable semicircles. The one at higher frequency (to the left) is attributed to the grain boundary resistance, with the bulk resistance the intercept at high frequency (125 Ω). The semicircle at lower frequency (to right) is attributed to the resistance between the LICGC and the conductive paste. With increasing temperature, the two semicircles form one broadened semicircle, with the high frequency intercept still the bulk resistance of 125 Ω and a conductivity of 1.5×10^{-4} S/cm at 30 °C, in agreement with data provided by the supplier (Ohara Inc).

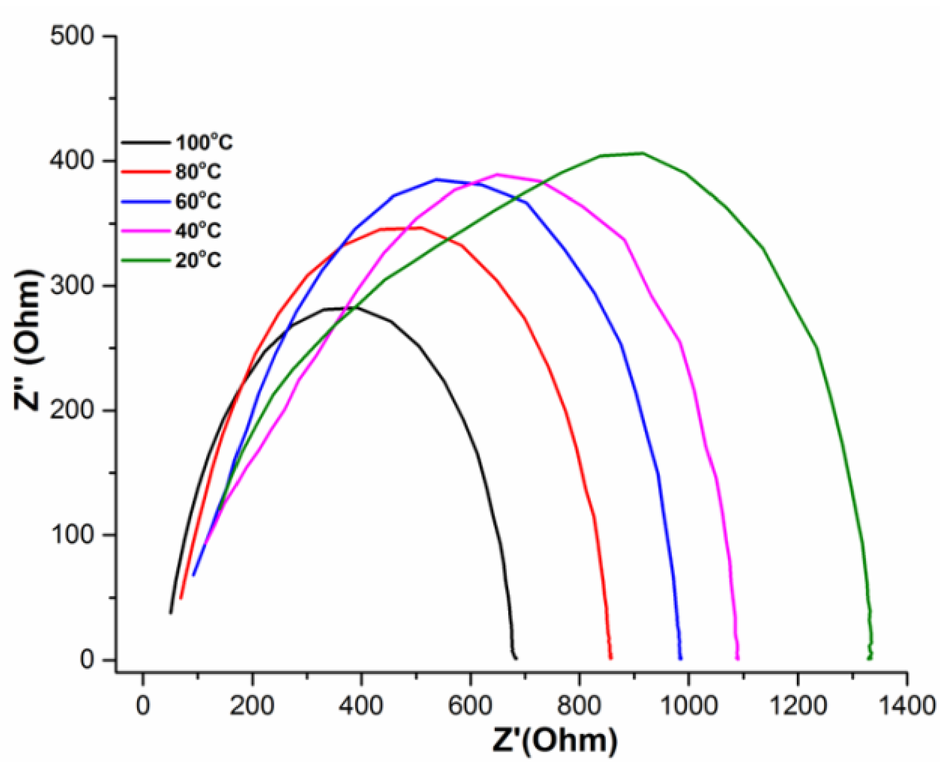
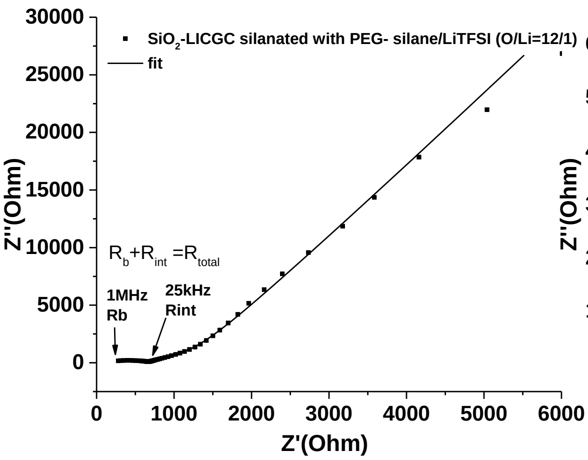
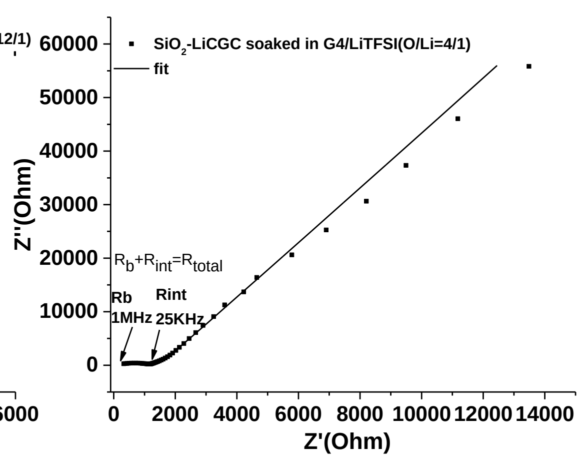


Figure S5. Z′′ vs Z′ for the LICGC, which was Li_2O-Al_2O_3-SiO_2-P_2O_5-TiO_2-GeO_2, with a proprietary composition (Ohara glass, Corp.) as a function of temperature

EIS data with stainless steel blocking electrodes for the SiO_2-LICGC infused with: (i) G_4, (ii) G_4/LiTFSI (O/Li = 4/1) and (iii) silanated with PEG-silane/LiTFSI (O/Li = 12/1)

The EIS data obtained with blocking stainless steel electrodes (examples shown below) were analyzed using the equivalent circuit shown in **Figure S6**. For these samples, there was good contact with the stainless steel electrodes (unlike the LICGC disc that required carbon paste for adhesion). The Nyquist plots of SiO_2-LiCGC with (i) G_4; (ii) G_4/LiTFSI; and (iii) silanated with PEG-silane/LiTFSI (O/Li=12/1), shown below for (ii) and (iii) have similar features. All plots have two resistive components, one at high frequency (at 1MHz) and the other at low frequency (around 25 KHz). The high and low frequency intercepts are attributed to the bulk resistance of LiCGC and the interface resistance of LiCGC-SiO_2 soaked with G_4LiTFSI or silanated with PEG silane/LiTFSI (O/Li=12/1), respectively. The calculated capacitance values from equivalent circuit fitting for the bulk and interface resistances were in the range 10^{-12} to 10^{-8} F/cm^2 and 10^{-7} to 10^{-5} F/cm^2, respectively. Capacitance values in these ranges are known to correspond to bulk and interfacial impedances[1, 2]. The assignment of the interface resistance of SiO_2-LiCGC was further checked by incorporating pure G_4 (no salt) in the LICGC-SiO_2. Pure G_4 increased (doubled) the interface resistance at 30°C, confirming that this frequency region corresponded to the interface resistance.





Equivalent circuit used:

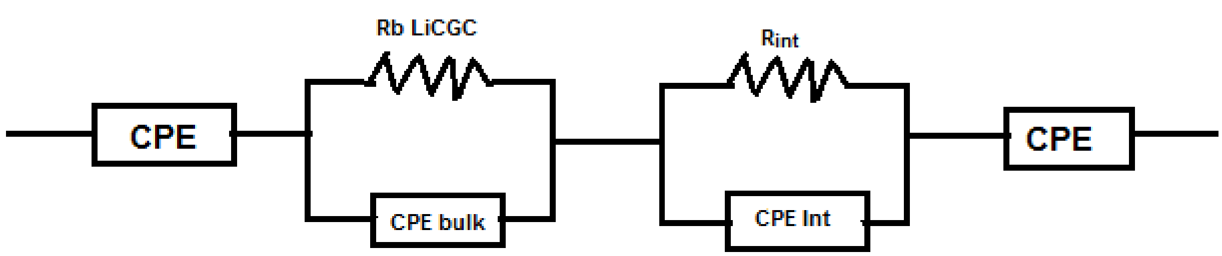
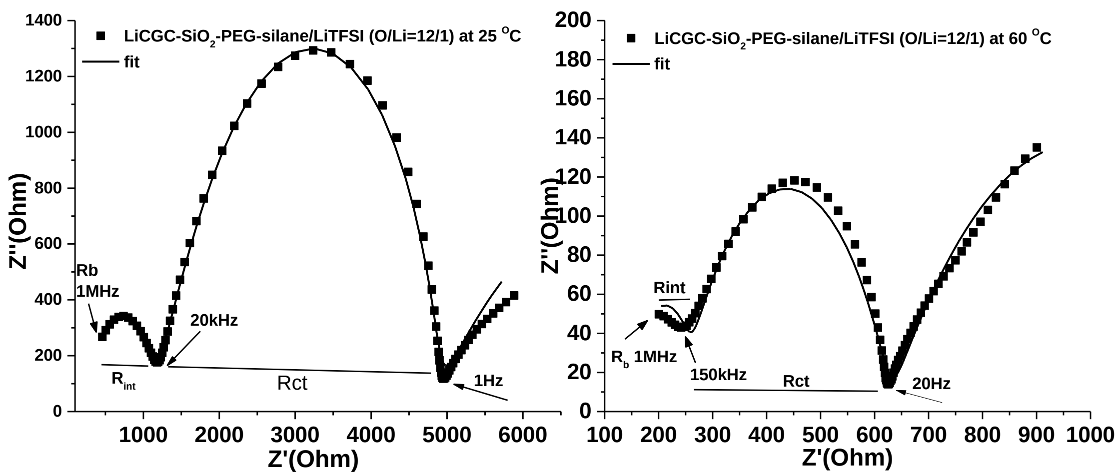


Figure S6. Equivalent circuit used to analyze EIS data with stainless steel blocking electrodes.

- CPE is the double layer capacitance at the electrolyte/blocking electrode interfaces;
- R_b is the bulk resistance of the LICGC;
- R_{Int} is the interfacial resistance between the LiCGC and SiO_2 infused with LiG_4TFSI or between LiCGC and SiO_2 silanated with PEG- silane/ LiTFSI (O/Li=12/1)

EIS data with Li^0 electrodes for SiO_2-LICGC : (i) soaked with G_4 (ii) soaked with G_4LiTFSI or (iii) silanated with PEG-silane/LiTFSI (O/Li=12/1)

For Li^o non-blocking electrodes, the EIS spectra of SiO_2-LICGC silanated with PEG-silane/LiTFSI (O/Li = 12/1) or soaked with G_4LiTFSI, were analyzed using the equivalent circuit shown in **Figure S7**). The Nyquist plots of SiO_2-LiCGC soaked with LiG_4TFSI or silanated with PEG-silane/LiTFSI (O/Li=12/1) and G_4 (only 1 temperature obtained) have similar features, and are composed of three resistive elements. The example shown below is for SiO_2-LICGC silanated with PEG-silane/LiTFSI (O/Li=12/1) at 25 ^{0}C and 60 ^{0}C. There are two resistive components at high frequency (1MHz and 50 KHz at 25 ^{0}C) and one at low frequency (~ 1Hz at 25 0C). The 1MHz, 50KHz and 1Hz components are attributed to the bulk resistance of LICGC, the interface resistance between LICGC and SiO_2 silanated with PEG silane/LiTFSI (O/Li=12/1) and the charge transfer resistance with Li^o metal, respectively. The calculated capacitance values from equivalent circuit fitting for the bulk, interface and charge transfer resistances were in the range 10^{-12} to 10^{-8} F/cm^2 , 10^{-9} to 10^{-7} F/cm^2 and 10^{-7} to 10^{-5} F/cm^2 respectively, consistent with values typically observed for these processes[1, 2].



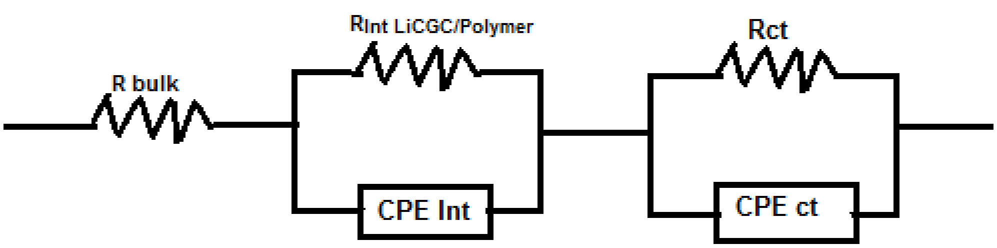


Figure S7. Equivalent circuit used for analysis of the EIS spectra with non-blocking Li^0 electrodes

- R_b is bulk resistance of the LICGC
- R_{Int} is interfacial resistance between the LICGC and SiO_2 incorporated with LiG_4TFSI, and between LICGC and SiO_2 silanated with PEG-silane/LiTFSI (O/Li=12/1)
- R_{CT} is the charge transfer resistance

Interfacial resistance at 60°C

Z′′ vs Z′ for Li^0 /separator/Li^0 (separator = SiO_2-LICGC silanated with PEG-silane/LiTFSI (O/Li = 12/1)) as a function of time at 60 ^{0}C. The EIS data at 60^0 has similar features (R_{bulk}, $R_{interface}$, R_{ct}) to that at 25 ^{0}C, as shown in **Figure 3C and Figure S8**. From **Figure 3C and S7**, it is evident that total resistance of the cell at 60 ^{0}C decreases by 13 fold compared with the total resistance at 25 ^{0}C. The high frequency intercept, which corresponds to the bulk resistance of the LiCGC at 25 ^{0}C and 60 ^{0}C, matches the bulk conductivity of the LICGC measured with carbon paste at the respective temperatures. The decrease in total resistance at high temperatures may be due to better wettability of the electrolyte in contact with the lithium metal at the higher temperature. The interface resistance of the SiO_2-LICGC silanated with PEG-silane/LiTFSI (O/Li = 12/1) decreased 6 fold at 60 ^{0}C compared with 25 ^{0}C. This is attributable to the decreased resistance of both LICGC and SiO_2 containing silanated PEG-silane in presence of LiTFSI (O/Li = 12/1) as the temperature increases.

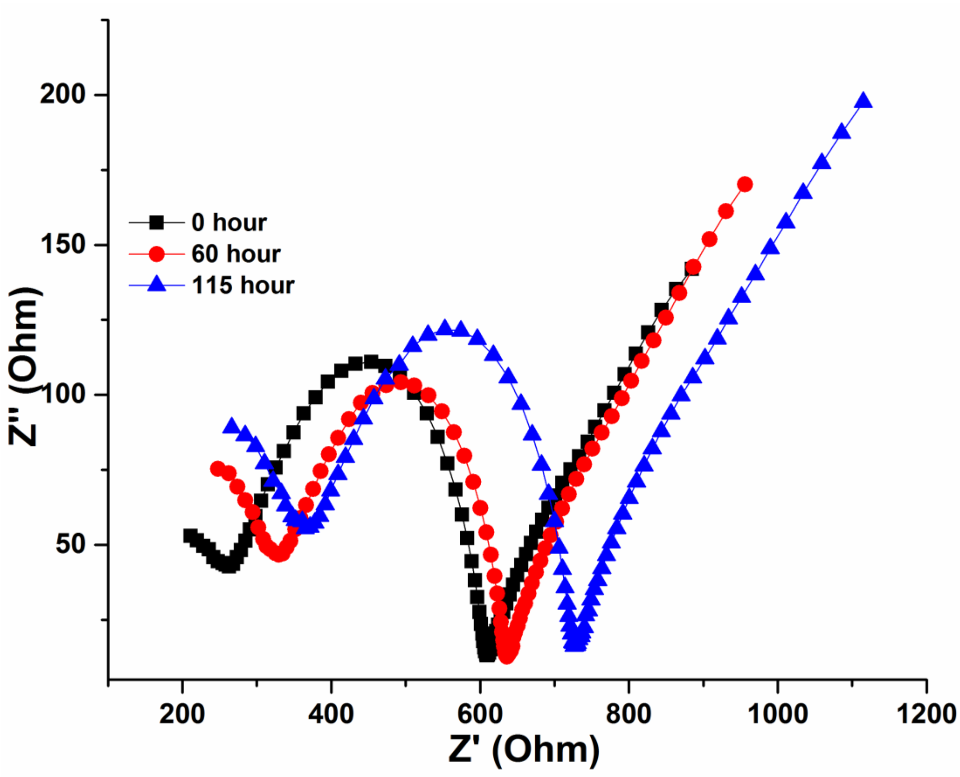


Figure S8. Z′′ vs Z′ as a function of time at 60 ^{0}C, Li^0 electrodes, 0.25 cm^2, for LICGC-SiO_2 silanated with PEG-silane/ LiTFSI (O/Li = 12/1)

1. Irvine, J. T. S.; Sinclair, D. C.; West, A. R., Electroceramics: Characterization by Impedance Spectroscopy. *Advanced Materials* **1990,** 2, (3), 132-138.
2. Huggins, R. A., Simple Method to Determine Electronic and Ionic Components of the Conductivity in Mixed Conductors A Review. *Ionics* **2002,** 8, (3-4), 300-313.