Supporting Information:

A new nanostructured γ-Li_3PO_4/GeO_2 composite for all-solid-state Li-ion battery applications

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Table S1. The resistances, capacitances and ideality factors (alpha) calculated from the fit of the impedance data of γ-Li_3PO_4/GeO_2 at different temperatures (equivalent circuit [R1Q1][R2Q2]Q3).

Temperature	R1 (Ω) Bulk resistance	R2 (Ω) Grain boundary resistance	Q1 parameters Capacitance and (α)	Q2 parameters Capacitance and (α)
40°C	840 349	946 943	5.0×10^{-11} (1.00)	3.5×10^{-10} (0.94)
60°C	173 463	112 802	5.1×10^{-11} (1.00)	3.6×10^{-9} (0.80)
80°C	45 273	29 702	6.3×10^{-11} (1.00)	1.7×10^{-8} (0.67)
100°C	17 352	9 070	2.8×10^{-10} (0.90)	1.5×10^{-8} (0.71)

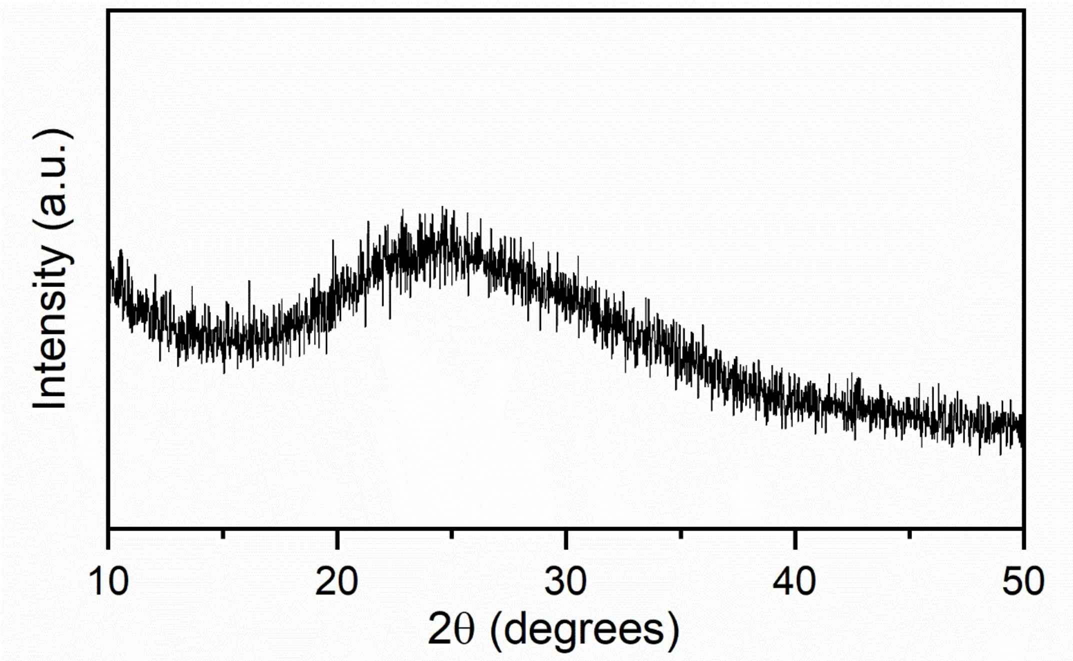

Figure S1. The XRD pattern of as-synthesized Li-P-Ge composite (microwave reaction; 260^oC) with no further calcinations.

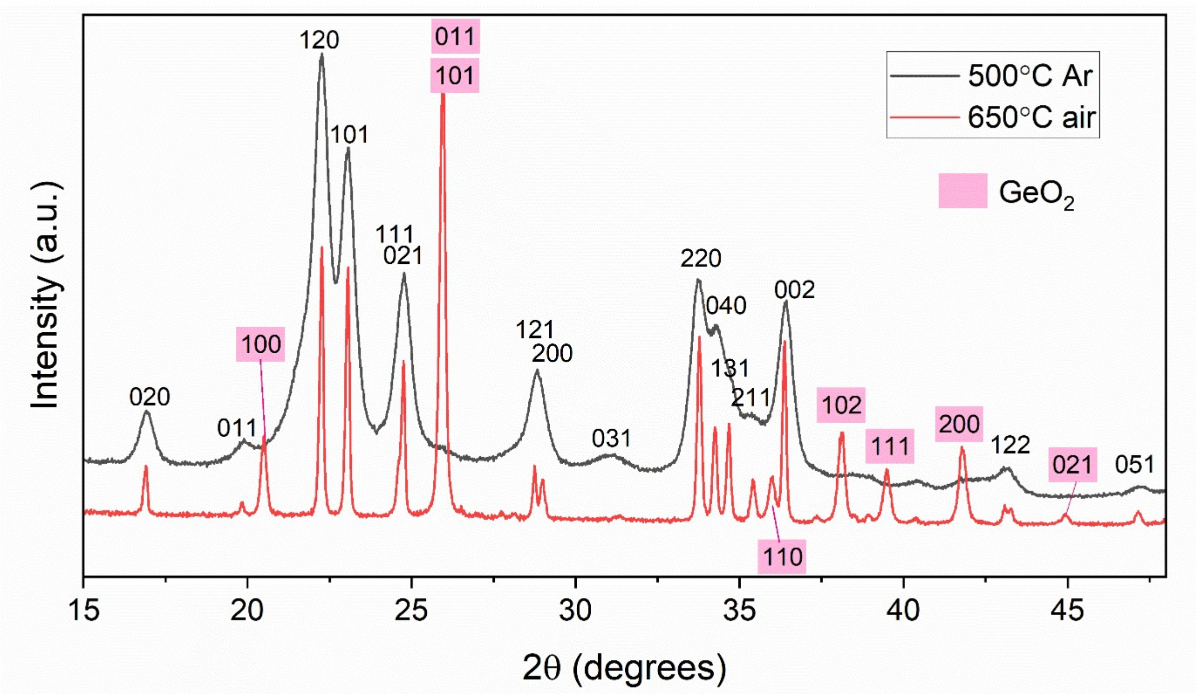

Figure S2. Indexed XRD data of γ-Li_3PO_4/GeO_2 samples calcined at 500^oC in argon and at 650^oC in air. Upon heating the material to 650^oC, no peak shifts were observed but the crystallinity was highly improved which allowed an accurate analysis of the XRD data.

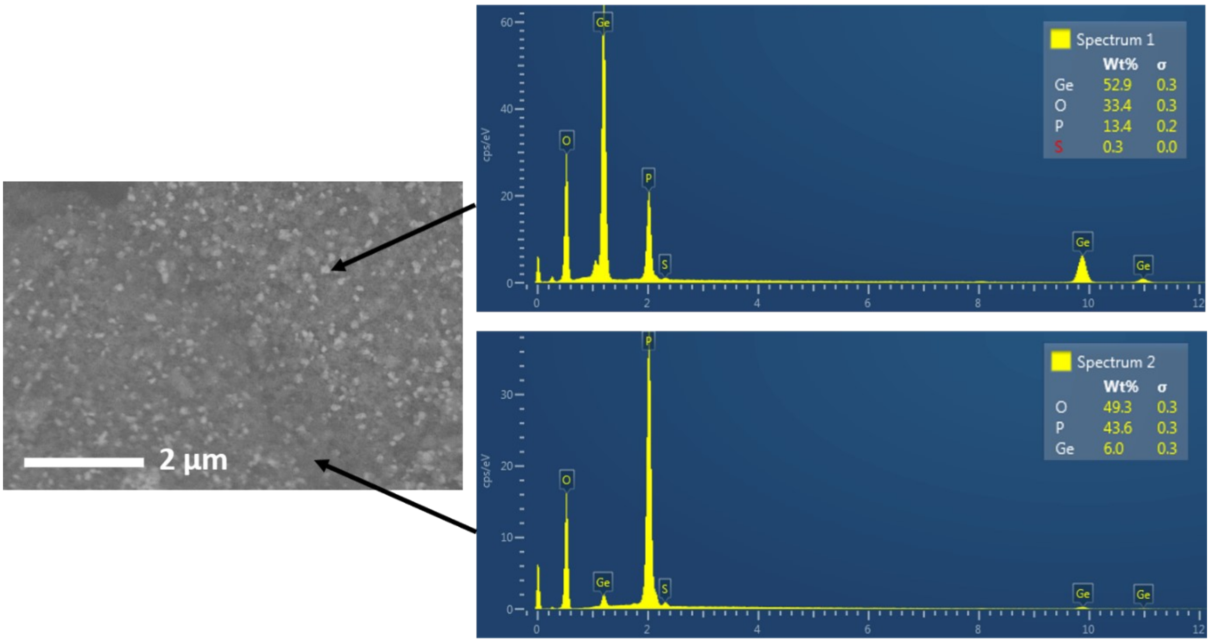

Figure S3. An EDX analysis of a sample of air-calcined γ-Li_3PO_4/GeO_2.

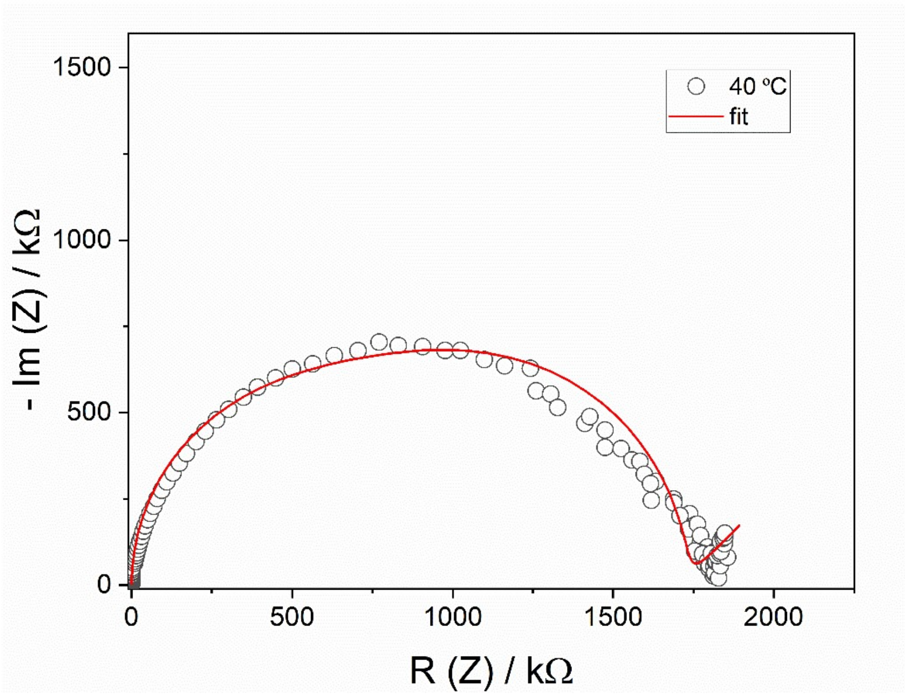

Figure S4. The impedance plot of argon-calcined γ-Li_3PO_4/GeO_2 at 40 °C, fitted using the [R1Q1][R2Q2][Q3] equivalent circuit.

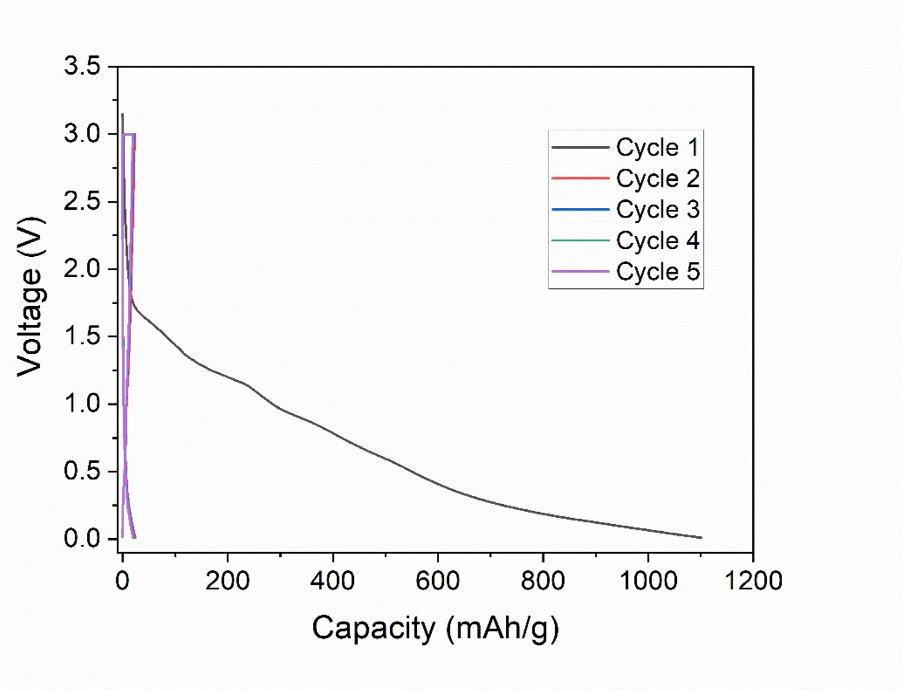

Figure S5. Charge/discharge curves (at 80 °C) for the first 5 cycles of the GeO_2-C/Li_3PS_4/Li cell at a rate of 150 mAh/g (with respect to the germanium metal content). Commercial GeO_2 (Alfa Aesar; 99.99%) was mixed with carbon black (15 wt%) then employed in the three-layer cell by pressing the cell components at ~250 MPa.

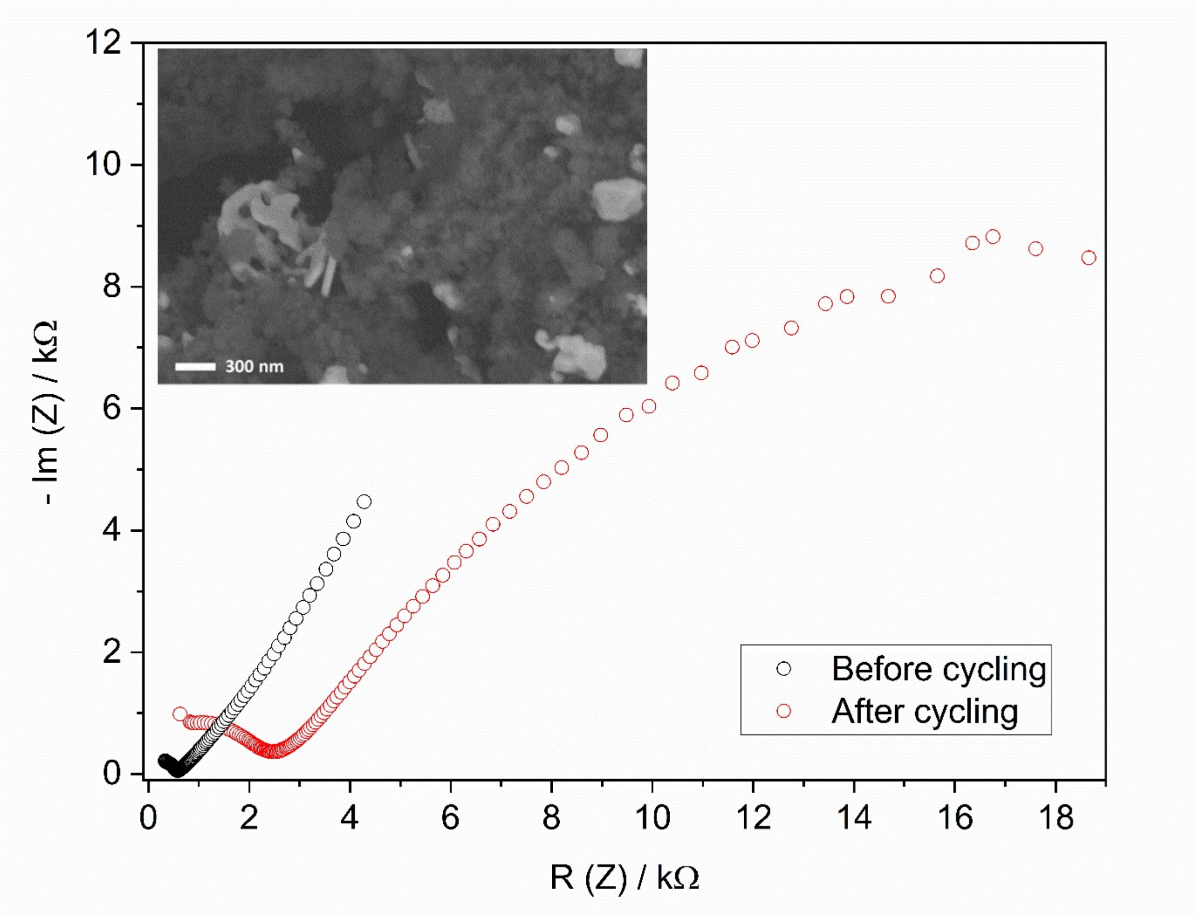

Figure S6. Typical impedance plots collected (at 80^{o}C) from an Li_3PO_4-GeO_2-C/Li_3PS_4/Li solid-state cell before and after cycling. The inset is an SEM image collected from the γ-Li_3PO_4/GeO_2 composite after cycling, showing Ge nanoparticles distributed in a matrix of nanostructured γ-Li_3PO_4/C..