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Supplementary Information

Study on $LiFePO_4$/graphite cells with built-in $Li_4Ti_5O_{12}$ reference electrodes

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Figure

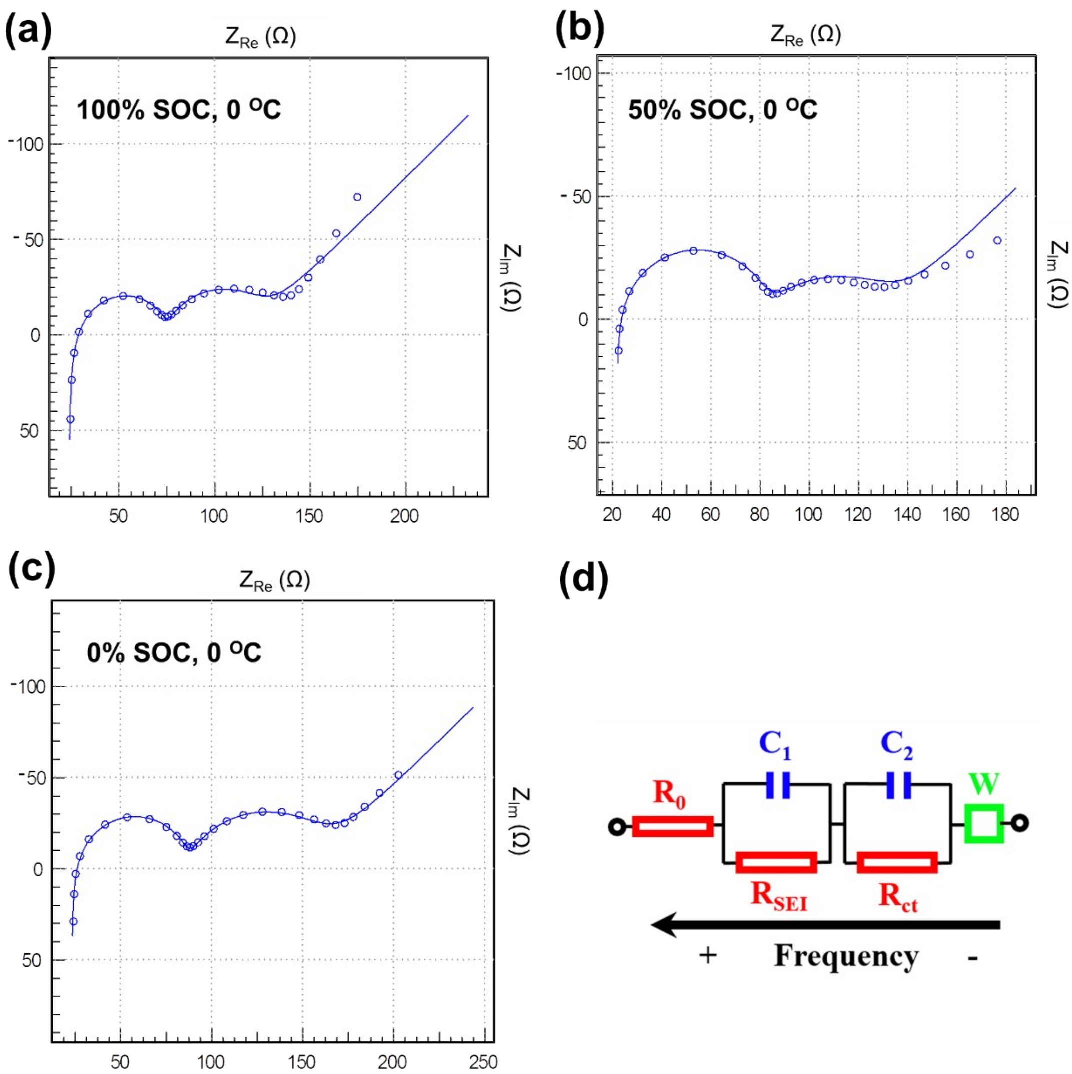

Fig. S1† (a-c) Nquist plots of the fabricated cells at different state of charge (SOC) tested at 0 °C; (d) The simplifed equivalent circuit for Nquist plots.

As can be seen in Fig. S1†, all the impedance plots of the fabricated cells at different state of charge (SOC) tested at 0 °C using LTO as reference electrode consisted of two depressed semicircles in the high-to-medium frequency region and a slopping line in the low frequency region. The first semicircle is related to the Li^+ transport through the solid electrolyte interface (SEI) film, and the second one is related to the charge transfer reactions; the slopping line corresponded to the Li^+ diffusion process. The plots were fitted by the simplified equivalent circuit given in Fig. S1d†, where R_0 represents the ohmic resistance (the intersection at high frequency with Z_{Re} axis in the Nyquist plots), R_{SEI} and C_1 correspond to the SEI film resistance and the relax capacitance (the high-frequency region of the semicircle in the Nyquist plots), R_{ct} and C_2 relate to the charge transfer resistance and the double layer capacitance (the medium frequency region of the semicircle in the Nyquist plots), and W denotes the Warburg resistance associated with Li^+ diffusion process (the slanted line in the low-frequency region of the Nyquist plots).

The other Nquist plots of the fabricated cells at different state of charge (SOC) and temperature using LTO as reference electrode have similar phenomenon and explanation. The corresponding fitting results using the simplified equivalent circuit shown in Fig. S1d† were listed in Table 1 and Table 2.

Table

Table S1† Comparison of the LTO reference electrode with the others in the previous reports.

Reference electrode	Advantages	Disadvantages	Reference number
Metal lithium in half coin cells and Swagelok cell	Simple; Can measure both the positive or negative electrodes directly.	Active in air; Cells must be fabricated in glove-box filled with inert gas; Not stable at low temperature.	1
Metal Lithium in three-electrode cells	Facile; Can measure both the positive and negative electrodes directly.	Active in air; Cells must be fabricated in glove-box filled with inert gas; Not stable at low temperature.	8
Lithium-preloaded $Li_{4/3}Ti_{5/3}O_4$	Stable at wide temperature range compared with metal lithium electrode.	The synthase process is quite hard.	2
Metal lithium micro-reference electrode on insulation-coated copper wire	Stable at low temperature compared with metal lithium electrode.	The fabrication process is relatively complex.	9
Li_yS_n alloy	Relatively stable at room temperature.	Active in air; Cells must be fabricated in glove-box filled with inert gas; The fabrication process is relatively complex.	4
$Li_4Ti_5O_{12}$ (LTO)	Easy for fabrication; Stable at wide temperature range; In situ measurement for both positive and negative electrode; Rechargeable to keep the potential stable for long time measurement.	The LTO reference electrode is fabricated in a cell, which would occupy some space in the testing cell.	This work