Supplementary information

Li$_5$Cr$_7$Ti$_6$O$_{25}$ as a Novel Negative Electrode Material for Lithium-Ion Batteries

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In this study, we synthesized Li$_5$Cr$_7$Ti$_6$O$_{25}$ and reported the electrochemical performance in a wide voltage range of 0-2.5 V. The higher working potential of Li$_5$Cr$_7$Ti$_6$O$_{25}$ (at about 1.5 V) compared with other negative electrodes also limits the application Li$_5$Cr$_7$Ti$_6$O$_{25}$ for high energy density devices because energy density is basically defined as the product of capacity and working potential. In this study, we found that Li$_5$Cr$_7$Ti$_6$O$_{25}$ can be lithiated to the state Li$_{13}$Cr$_7$Ti$_6$O$_{25}$ (discharged to 0 V), which provides a theoretical capacity that is about 2.2 times higher than that of the compound lithiated to Li$_{11}$Cr$_7$Ti$_6$O$_{25}$. The discharge behavior of Li$_5$Cr$_7$Ti$_6$O$_{25}$ down to 0 V can increase the energy density and discharge capacity due to the lower discharge potential. Lithium-ion batteries have a risk of explosion from possible inner short circuit. An internal short is much more dangerous than an external short circuit, because the former induces an enormous heat instantaneously and locally to cause thermal

runaway of the electrolyte and electrode materials[**Ref.:** M.-S. Wu, P.-C. Julia Chiang, J.-C. Lin and Y.-S. Jan, *Electrochim. Acta*, 2004, **49**, 1803]. Upon short circuit or abuse, partial negative electrode materials in the electrode are overlithiated and may hold more lithium ions than those in the initial materials. Therefore, it is important to study the over-discharge behaviors of negative electrode materials at lower voltage considering the safety.

With theses consideration mentioned above, we synthesized $Li_5Cr_7Ti_6O_{25}$, and reported the electrochemical performance discharged to 0 V.

1. Experimental

1.1 Synthesis of $Li_5Cr_7Ti_6O_{25}$

$Li_5Cr_7Ti_6O_{25}$ powders were prepared by a facile sol-gel process. A required amount of $CH_3COOLi \cdot 2H_2O$ were dissolved in an appropriate quantity of aqueous alcohol (Solution A). A required amount of $Cr(NO_3)_3 \cdot 9H_2O$ (AR), and $Ti(C_4H_9O)_4$ (AR) were dissolved in an appropriate quantity of alcohol (Solution B). The solution (Solution B) was stirred at room temperature and the triethanolamine (TEA) and Solution A were added to the solution which acts as chelating agent in the polymeric matrix. The temperature of the mixed solution was raised to about 80 °C and continued stirring till the solution turned into high-viscous gel. The resulted gel was dried at 80-90 °C for 24 h. The precursor powder was ground to fine powder and sintered at 600 °C under air flowing conditions with a constant heating followed by cooling rate at 5 °C min^{-1} to decompose organic constituents. The sintered powder was ground to a fine powder and re-sintered successively at 800 °C for 12 h and heating and cooling rate was maintained at 5 °C min^{-1}.

1.2 Material characterizations

The phase purity was verified from powder X-ray diffraction (XRD) measurements. The particle morphology of the powders after sintering was obtained using a scanning electron microscopy (SEM).

FT-IR spectroscopy of the samples was performed using a Nicolet Nexus 6700 FT-IR spectrophotometer with a resolution of 4 cm^{-1}. A total of 1.5 mg sample dried at 120 °C was thoroughly mixed with 200 mg KBr and pressed into pellets and the scans were performed immediately to avoid water absorption. The frequency range was 1000–400 cm^{-1}.

1.3 Electrochemical characterizations

Electrochemical characterizations were performed by using CR2025 coin-type cells. The electrode was prepared by blending a ball-milled mixture of 80% active material and 10% SP carbon with 10% polyvinylidene fluoride dissolved in N-methyl-2-pyrrolidone. The electrode slurry thus obtained was coated on Cu foil and dried overnight under vacuum at 120 °C. The thickness of electrode prepared in this study is about 30 μm. The cells were assembled and sealed in an argon-filled glovebox with lithium foil as the   negative electrode and 1 M LiPF$_6$ dissolved in EC/DMC (1:1 by volume) as the electrolyte. Cyclic voltammetry (CV) test was carried out on a CHI 1000C electrochemical workstation with a voltage between 0.0 and 2.5 V at a scanning rate of 0.2 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) is measured by a PARSTAT 4000 electrochemical working station over a frequency range from 0.01 Hz to 10 kHz at a potentiostatic signal amplitude of 5 mV. The cells thus fabricated were cycled galvanostatically in the voltage range between 0.0 and 2.5 V, 1.0 and 2.5 V versus lithium using multichannel Land Battery Test System (Wuhan Jinnuo, China) at room temperature.
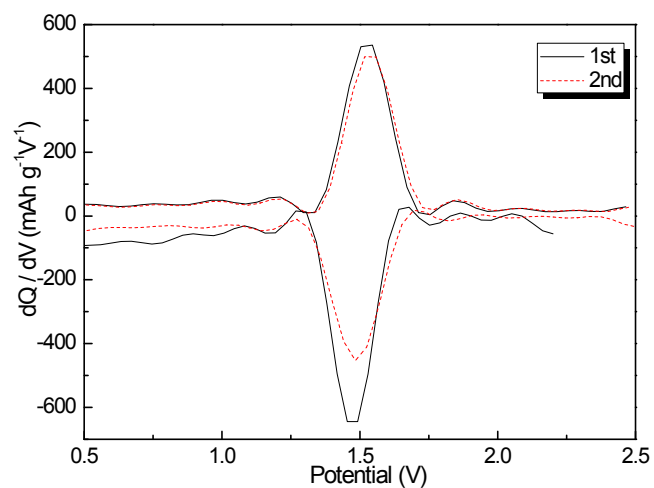
2. Supplementary figures

Fig. S1 − The first and second charge–discharge characteristics curves and differential capacity vs

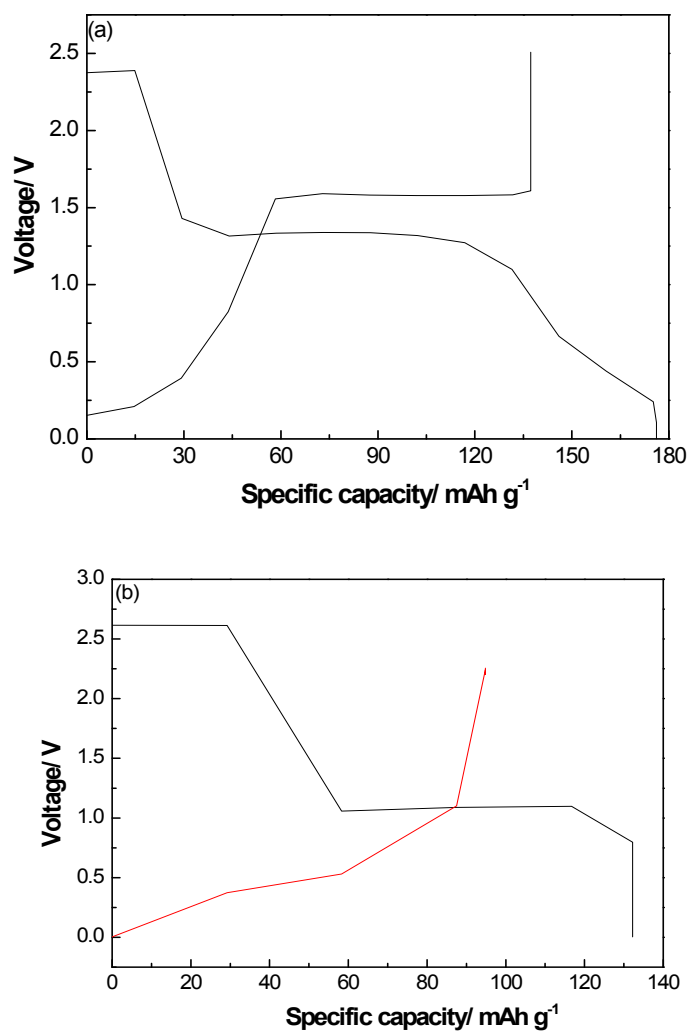voltage plots of coin cells carried out galvanostatically between 0 and 2.5 V.

Fig. S2 −Initial charge–discharge profiles of $Li_5Cr_7Ti_6O_{25}$ at (a) 5 C and (b) 10 charge–discharge

rates between 0 and 2.5 V. The charge rate and discharge rate are the same.

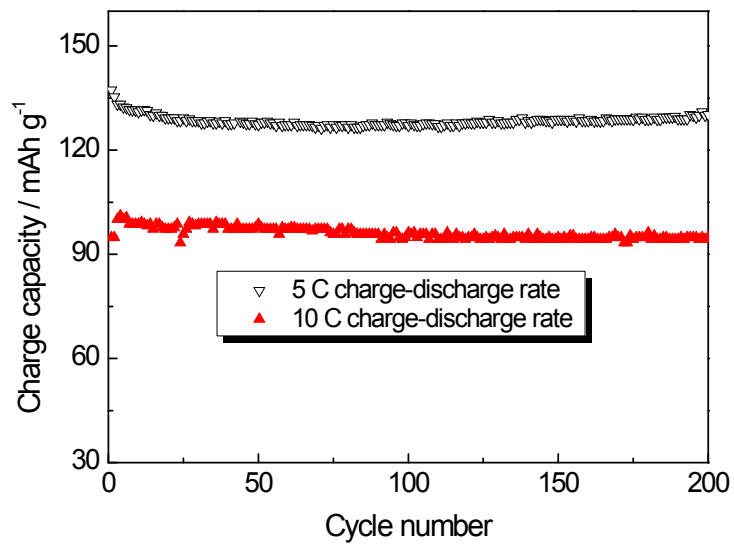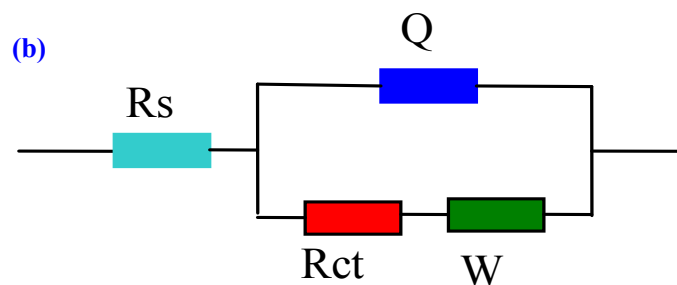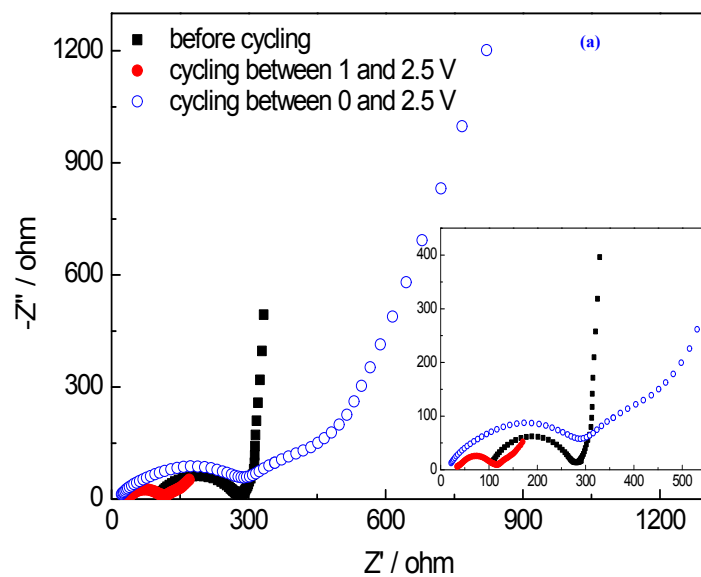**Fig. S3** −Charge capacity of $Li_5Cr_7Ti_6O_{25}$ at 5 C and 10 C charge-discharge rates. The charge and discharge rates are the same.

(c)

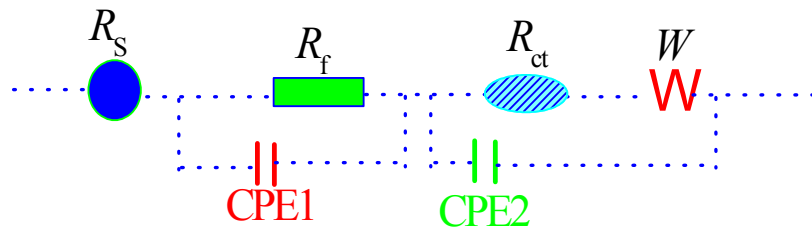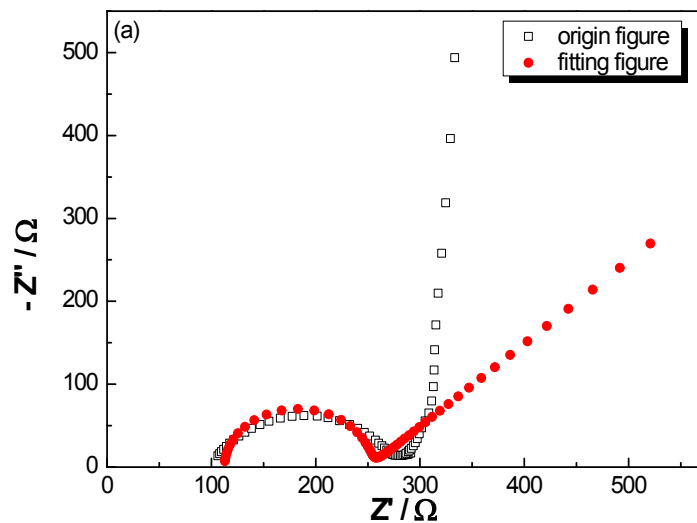**Fig. S4 −** (a) Nyquist plots for the $Li_5Cr_7Ti_6O_{25}$ with and without cycling; (b) Equivalent circuit used to analyze the EIS of $Li_5Cr_7Ti_6O_{25}$ cycled between 1 and 2.5 V; (c) Equivalent circuit used to analyze the EIS of $Li_5Cr_7Ti_6O_{25}$ before cycling and cycled between 0 and 2.5 V. $Li_5Cr_7Ti_6O_{25}$ was cycled between 1 and 2.5 V at 0.2, 0.5, 1, 3, 5, and 0.2 C charge-discharge rates after 120 cycles, and then tested EIS. $Li_5Cr_7Ti_6O_{25}$ was cycled between 0 and 2.5 V at 10 C charge-discharge rates after 200 cycles, and then tested EIS.

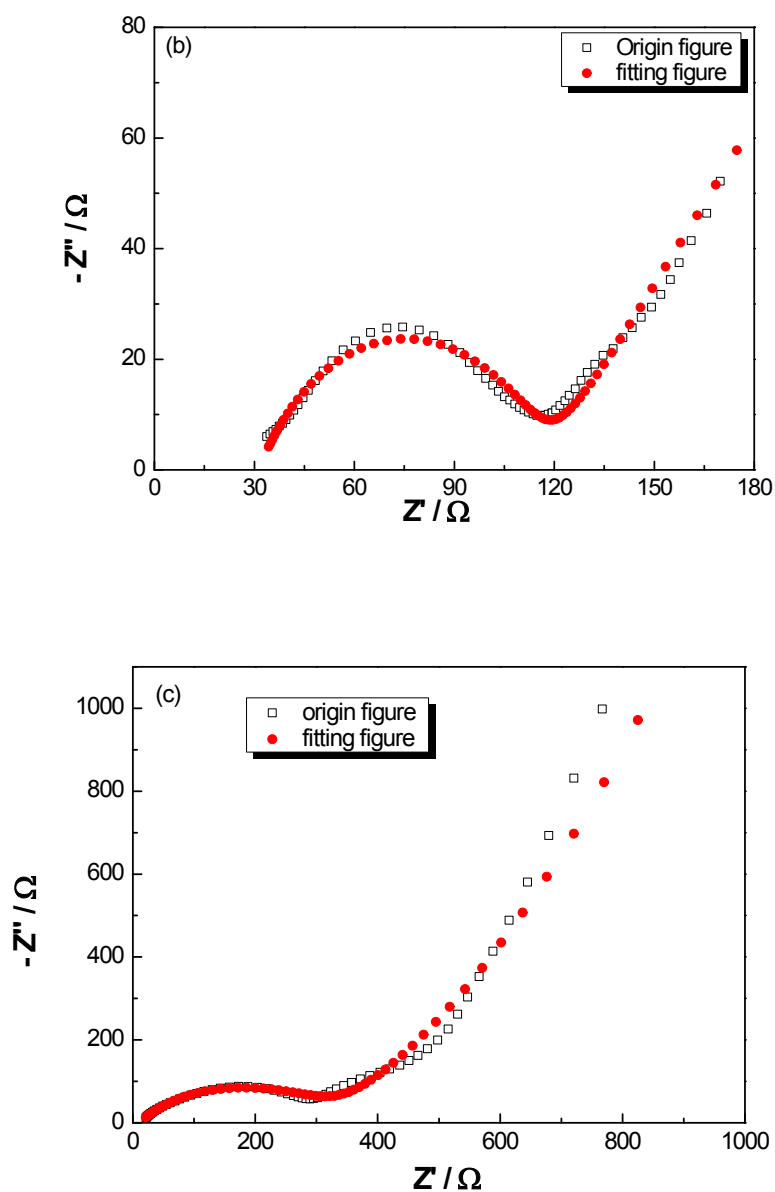**Fig. S5** − Nyquist plots and fitting figures for the $Li_5Cr_7Ti_6O_{25}$ with and without cycling (a) fresh $Li_5Cr_7Ti_6O_{25}$ electrode, (b) $Li_5Cr_7Ti_6O_{25}$ cycled between 1 and 2.5 V; (c) $Li_5Cr_7Ti_6O_{25}$ cycled between 0 and 2.5 V. $Li_5Cr_7Ti_6O_{25}$ was cycled between 1 and 2.5 V at 0.2, 0.5, 1, 3, 5, and 0.2 C charge-discharge rates after 120 cycles, and then tested EIS. $Li_5Cr_7Ti_6O_{25}$ was cycled between 0 and 2.5 V at 10 C charge-discharge rates after 200 cycles, and then tested EIS.

The small semicircle appearing in the high-frequency region reflects the resistance (R_f) of migration of Li^+ ions through the surface films, and film capacitance (CPE1).[S1] The middle-frequency capacitive loop is caused by charge transfer resistance (R_{ct}) and interfacial capacitance

(CPE2). The low-frequency straight line can be attributed to diffusion of Li^+ ions in the samples. [S2] R_S is the solution ohmic resistance of the electrode system; R_f and CPE1 are, respectively, the resistance and capacitance of a solid electrolyte interphase (SEI) film, and W is the Warburg impedance of solid-phase diffusion [S3].

References

S1 M.D. Levi, D. Aurbach, *J. Phys. Chem. B*, 1997, 101, 4630-4640.

S2 L. Pan, X.-D. Zhu, X.-M. Xie and Y.-T. Liu, *J. Mater. Chem. A*, 2015, **3**, 2726–2733.

S3 H. Li, L. Shen, K. Yin, J. Ji, J. Wang, X. Wang and X. Zhang, *J. Mater. Chem. A*, 2013, **1**, 7270-7276.

Table S1 Some data of the $Li_5Cr_7Ti_6O_{25}$ sample with and without cycling obtained by EIS fitting

Parameters	Before cycling	Cycling between 1 and 2.5V at different rates after 120 cycles	Cycling between 0 and 2.5 V at 10 C rates after 200 cycles
R_s / Ω	112.6	31.3	11.13
R_{ct} /Ω	138.9	86.59	317.1