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Supporting information

Nanoscale spinel $LiFeTiO_4$ for intercalation pseudocapacitive Li^+ storage

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Table S1. XRD Rietveld refinement parameters of the as-prepared $LiFeTiO_4$

		Fd*-3*m **spinel $LiFeTiO_4$**	***Fd*-3*m*** **spinel Fe_2TiO_4**	***Fm*-3*m*** **rock-salt FeO**
a / Å		8.354(3)	8.463(3)	4.243(6)
V / Å^3		583.1	606.2	76.4
wt%		75.0	23.2	1.8
D / nm		3.3	7.2	30.5
(*x*,*y*,*z*)/occ.				
	O1	0.2599/1.000	0.2577/1.000	0.5/1.000
	Fe1	0.125/0.300(5)	0.125/0.828(7)	0/1.000
	Li1	0.125/0.699(9)		
	Fe2	0.5/0.036(2)	0.5/0.276(0)	
	Li2	0.5/0.463(8)		
	Ti1	0.5/0.500(1)	0.5/0.724(8)	
	Fe3	0/0.121(7)		

Table S2. Mössbauer parameters of as-prepared and cycled $LiFeTiO_4$: iron oxidation state (n^+), isomer shift (IS/mm s^{-1}), quadrupole splitting (QS/mm s^{-1}), linewidth (Γ/mm s^{-1}), relative intensity

Samples	**Fe^{n+}**	**IS**	**QS**	**Γ**	**%**
as-prep	3+	0.32	0.64	0.50	47.8
	3+	0.35	1.10	0.47	15.8
	2+	1.11	1.41	0.59	16.7
	2+	0.74	1.09	0.66	19.6
1^{st}-4.8V (R.T.)	3+δ	0.19	0.66	0.41	26.5
	3+	0.40	0.72	0.43	38.1
	2+	0.81	0.89	0.69	23.7
	2+	0.95	1.85	0.57	11.7
160^{th}-4.8V (40°C)	3+δ	0.16	0.72	0.34	21.0
	4+	0.04	0.16	0.19	4.3
	3+	0.36	0.74	0.41	36.7
	2+	1.10	1.55	0.70	17.8
	2+	0.61	0.80	0.67	20.2
100^{th}-1.5V (R.T.)	2+	0.99	1.38	0.75	49.9
	2+	0.99	2.14	0.45	42.5
	3+	0.30	0.29	0.32	7.6

Table S3. Refined lattice parameters of the major phase (cubic spinel *Fd*-3*m*) for the as-prepared and cycled $LiFeTiO_4$

	***a* / Å**	***V* / Å^3**	**Δ*V* %[a]**
as-prep	8.354(3)	583.2	0.0
100^{th}-1.5V (R.T.)	8.392(5)	591.1	+1.35
50^{th}-4.8V (40°C)	8.349(9)	582.2	-0.17
160^{th}-4.8V (40°C)	8.342(9)	580.7	-0.43
	8.044(8)[b]	520.6	-10.7%

[a] The lattice volume change (Δ*V* %) is given relative to the one of the as-prepared material.

[b] Lattice parameter corresponds to a newly formed cubic spinel phase.

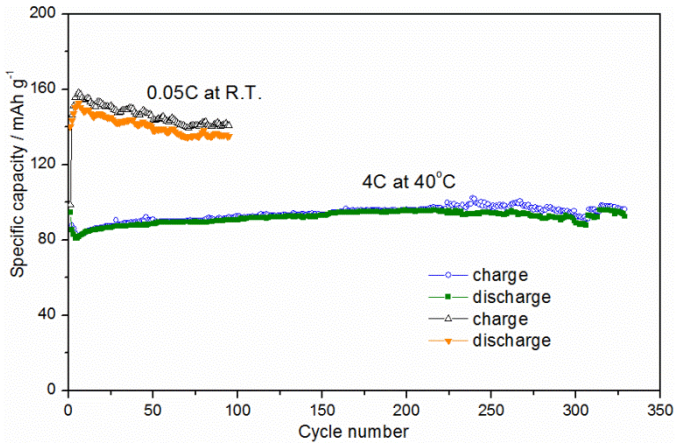

Fig. S1 Charge/discharge capacities of $LiFeTiO_4$ measured at a 0.05C rate at room temperature and at a 4C rate at 40 °C in the voltage range of 1.5–4.8 V vs. Li^+/Li.

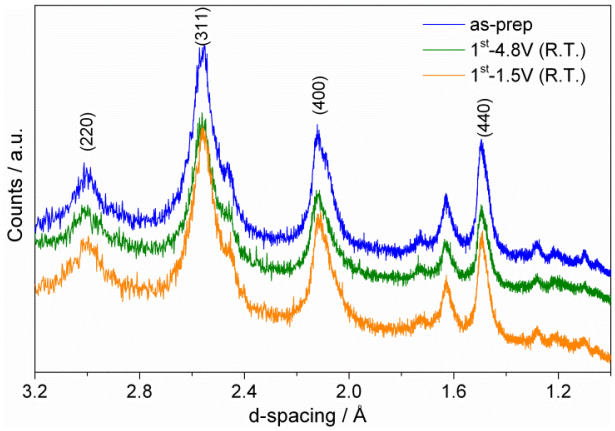

Fig. S2 *d*-spacing of as-prepared $LiFeTiO_4$ and samples collected from the first charge-discharge cycle at room temperature.

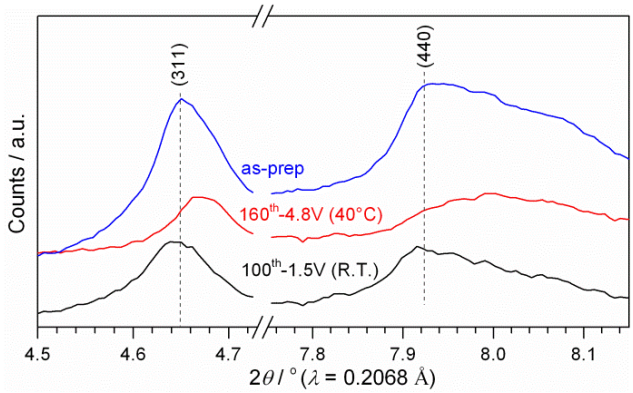

Fig. S3 *Ex situ* synchrotron XRD patterns of (311) and (440) Bragg peaks of as-prepared and cycled $LiFeTiO_4$.

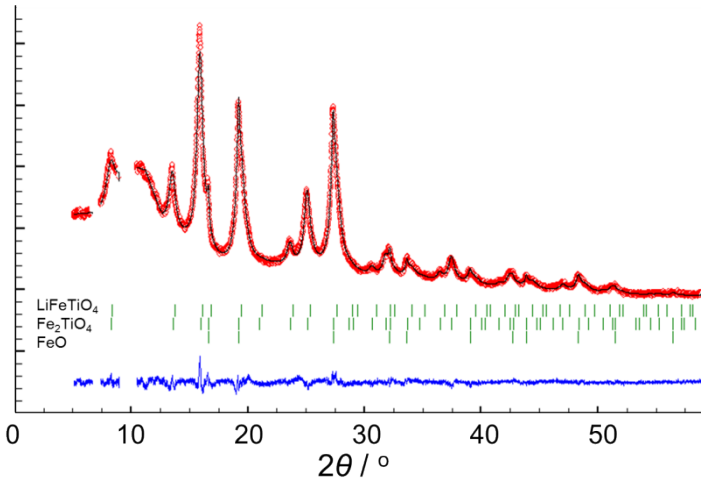

Fig. S4 Rietveld refinement of 100th discharged $LiFeTiO_4$. Space group: *Fd*-3*m*, *R*-factors: $R_p = 8.51$, $R_{wp} = 8.44$, $R_e = 6.30$. Fe^{3+} cations were distributed as: $(Fe_{0.11})_{8a}[Fe_{0.17}]_{16c}[Fe_{0.08}]_{16d}$ derived from the Rietveld refinement. Note that the Fe and Ti have very close X-ray scattering factors. The 2θ region at about 10^o was excluded for refinement.

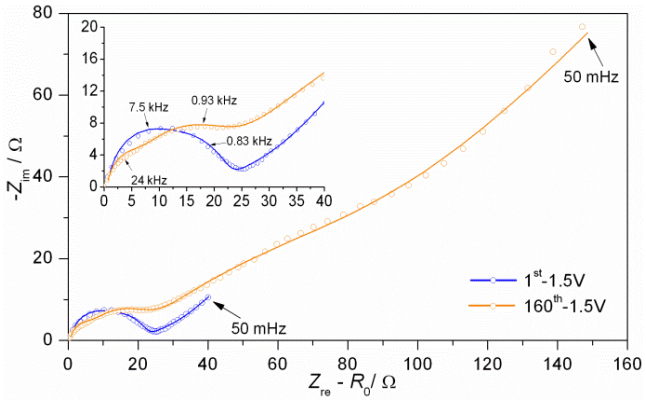

Fig. S5 Complex impedance plots of $LiFeTiO_4$ at fully discharged states (1.5 V) from the first and extended cycles tested at 40°C. Inset shows the enlarged plots at high frequent regions.