Supporting Information

Simple Approach: Heat Treatment to Improve the Electrochemical Performance of Commonly Used Anode Electrodes for Lithium-Ion Batteries

Ye Jin, Han Yu, Xinhua Liang *

Department of Chemical and Biochemical Engineering, Missouri University of Science and Technology, Rolla, Missouri 65409, United States

* Corresponding author. E-mail: liangxin@mst.edu

The following additional information is listed in this Supporting Information file, including Table S1, density data of the materials in electrodes; Table S2, weight percentages of F element of the electrodes; Table S3, electrochemical impedance spectra fitting results of electrodes; Table S4, binding energies and atomic concentrations of all cycled electrodes; Figure S1, FTIR spectra of PVDF before and after heat treatment and the TGA curve of PVDF; Figure S2, SEM images of pure active material powders or flakes; Figure S3, SEM images of fresh LTO electrodes with and without heat treatment; Figure S4, porosity and liquid electrolyte uptake of the electrodes with and without heat treatment; Figure S5, SEM image and EDS mapping of the cross-section area of the graphite electrodes; Figure S6, XPS survey spectra of all fresh electrodes; Figure S7, Nyquist plots of the electrodes; Figure S8, cycling performance of LTO and TiO_2 within 1.0- 3.0 V; Figure S9, CV curves of electrodes at different scan rates; Figure S10, XPS survey spectra of the cycled electrodes; Figure S11, SEM images of fresh LTO electrode without heat treatment; Figure S12, SEM image and EDS mapping of pristine LTO electrode after 500 cycles of charge/discharge; Figure S13, SEM images of fresh TiO_2 electrode with heat treatment; Figure S14, SEM image and EDS mapping of pristine graphite electrode after 500 cycles of charge/discharge; Figure S15, TEM images of pure TiO_2 nanoparticles.

Table S1. Density data of the materials in electrodes.

		Density (g cm^{-3})
Binder	PVDF	1.76
Conductive material	Carbon black	1.70
Active materials	TiO_2	3.78
	LTO	3.50
	Graphite	2.21

Table S2. Weight percentages of F element of the electrodes obtained from EDS spectra and XPS analysis.

Electrodes		F element (wt. %)	
		EDS spectrum	XPS analysis
LTO	Pristine	4.4	3.4
	250 ℃ treated	4.0	1.8
TiO_2	Pristine	4.8	3.5
	250 ℃ treated	4.6	3.1
Graphite	Pristine	-	2.5
	250 ℃ treated	-	2.4

Table S3. Electrochemical impedance spectra fitting results of electrodes after 1 C cycling performance test.

Electrodes		After formation				After long-term cycling			
		$R_f(\Omega)$	$R_{SEI}(\Omega)$	$R_{ct}(\Omega)$	$R_{tot}(\Omega)$	$R_f(\Omega)$	$R_{SEI}(\Omega)$	$R_{ct}(\Omega)$	$R_{tot}(\Omega)$
LTO	Pristine	8.6	39.6	164.6	212.8	20.1	183.6	492.9	696.6
	250 ℃ treated	6.0	55.2	101.2	162.4	25.2	103.4	290.1	418.7
TiO_2	Pristine	11.9	10.4	73.6	95.8	19.2	45.3	41.2	105.7
	250 ℃ treated	9.3	22.1	44.6	75.9	17.6	37.5	34.2	89.2
Graphite	Pristine	15.1	18.0	56.0	89.1	28.8	23.1	76.9	128.8
	250 ℃ treated	19.8	27.2	38.0	85.0	29.6	30.1	55.4	115.2

Table S4. Binding energies (BE) and atomic concentrations (at.%) of three anode materials with and without 250 °C treatment, identified by XPS at the surface of the electrodes.

Anode Material	Orbital	Pristine		250 °C treated		Assignment
		BE (eV)	at %	BE (eV)	at %	
LTO	F1s	684.4	42.8	684.3	56.0	LiF
		686.8	45.5	686.6	44.0	$LiPF_yO_z$
		687.8	11.7			PVDF
	C 1s	284.8	32.7	284.7	47.4	C-C
		286.4	7.4	286.4	13.3	CH_2
				288.6	4.3	Li_2CO_3
		289.9	60.0	289.7	35.1	CF_2
	O 1s	528.0	3.5	527.9	2.8	Ti-O from LTO
		529.6	3.5	529.9	8.1	ROLi
		531.5	93.0	531.4	89.1	C=O
TiO_2	F 1s	684.1	58.3	684.2	100.0	LiF
		686.7	19.2			$LiPF_yO_z$
		688.1	22.5			PVDF
	C 1s	282.7	6.6	282.7	1.2	Ti-C
		284.9	45.0	284.7	55.6	C-C
		286.4	18.5	286.2	18.6	CH_2
				288.7	12.4	Li_2CO_3
		290.1	30.0	290.3	12.1	CF_2
	O 1s	528.6	33.7	528.3	17.1	Ti-O from TiO_2
		530.5	8.8			ROLi
		532.0	57.5	531.4	82.9	C=O
Graphite	F 1s	683.7	33.4	684.1	59.2	LiF
		686.1	52.4	686.4	40.8	$LiPF_yO_z$
		687.0	14.2			PVDF
	C 1s	284.8	44.9	284.8	35.8	C-C
		286.4	21.4	286.4	16.5	CH_2
				288.4	7.7	Li_2CO_3
		289.7	33.6	289.8	40.0	CF_2
	O 1s			527.8	19.8	Li−O
		529.7	15.7	529.3	3.1	ROLi
		530.9	84.3	531.0	77.1	C=O

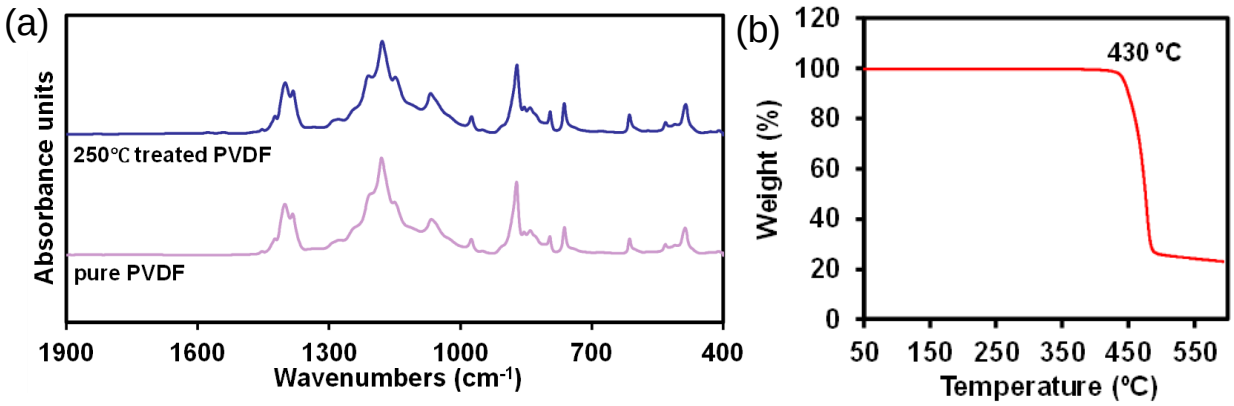

Figure S1. (a) FTIR spectra of PVDF before and after 250 °C treatment, and (b) TGA curve of the PVDF used in this study.

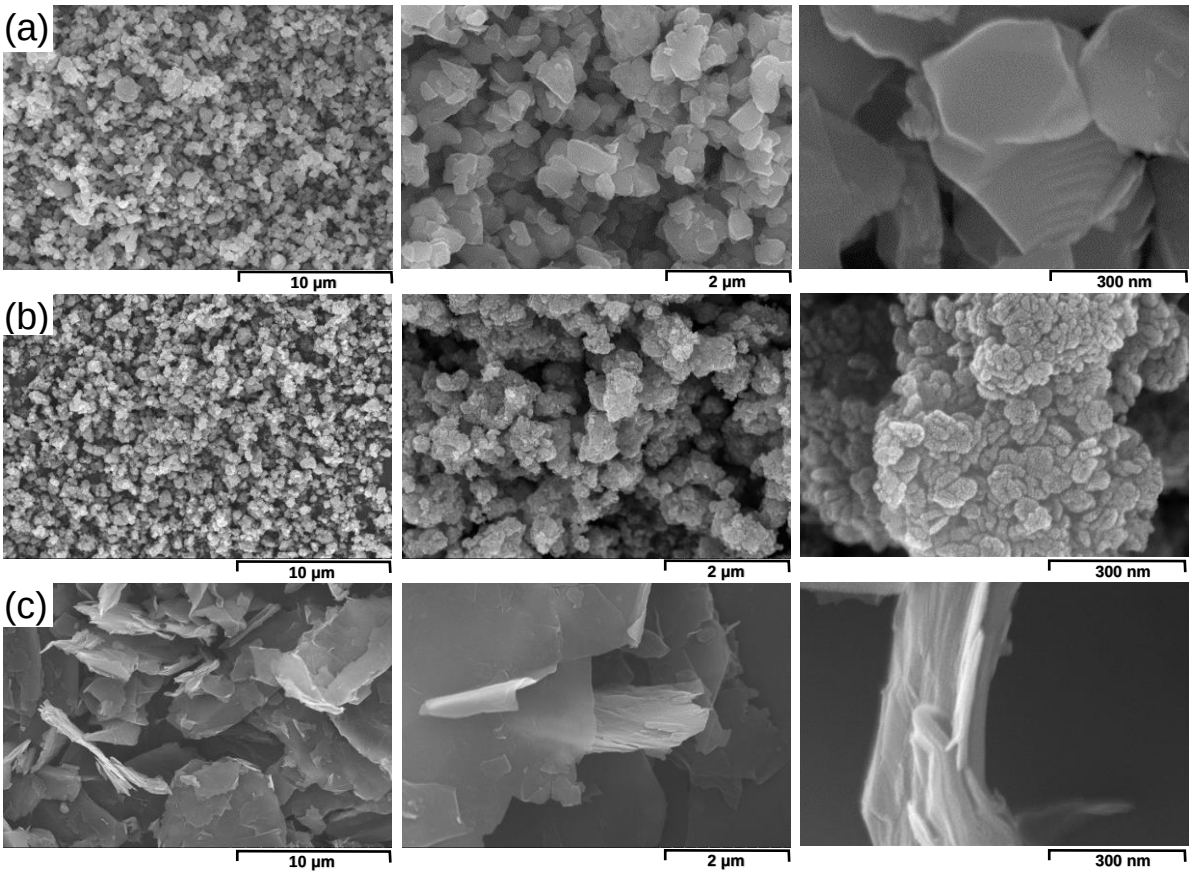

Figure S2. SEM images of (a) LTO powders, (b) TiO_2 powders, and (c) graphite flakes.

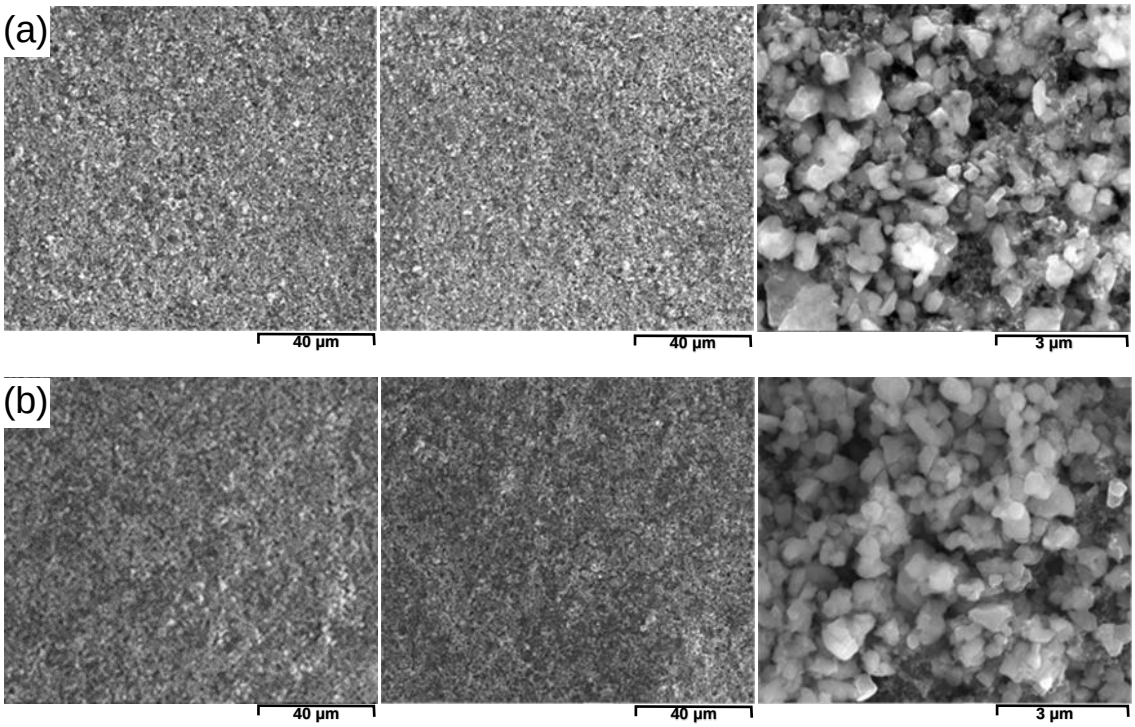

Figure S3. SEM images of fresh LTO electrodes (a) before and (b) after 250 °C heat treatment.

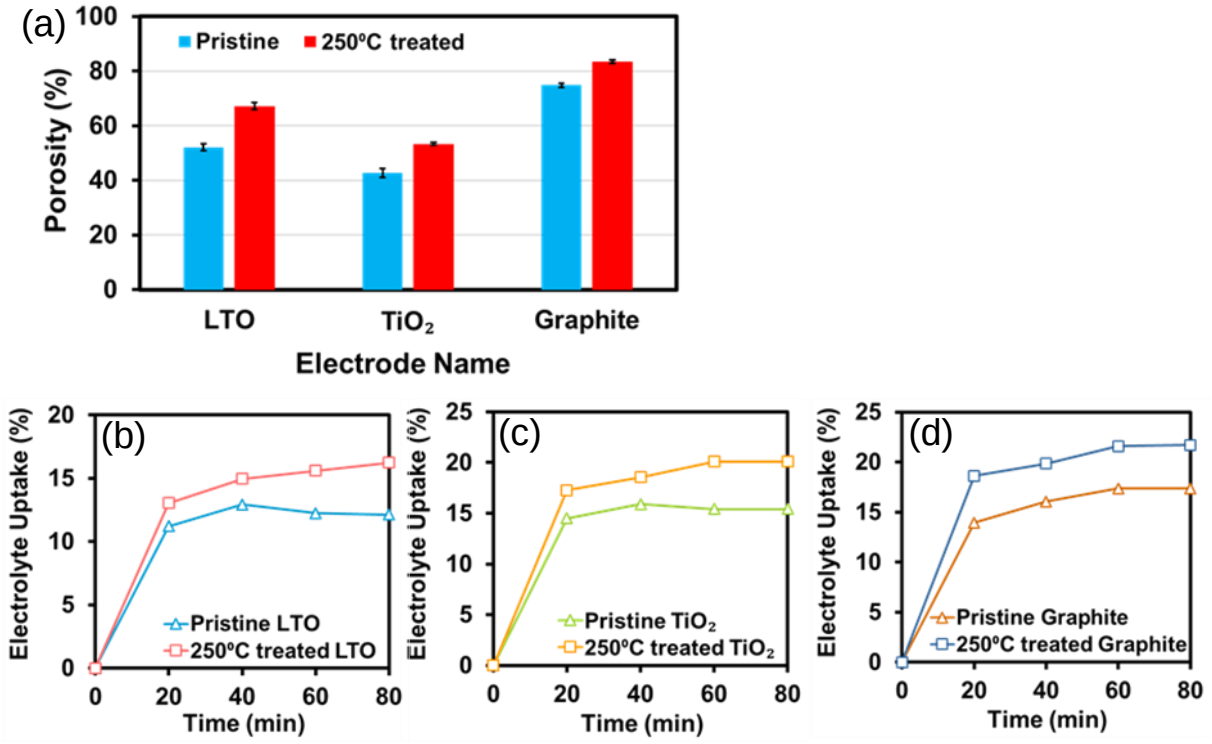

Figure S4. (a) Porosity of LTO, TiO_2, and graphite electrodes before and after 250 °C treatment. Liquid electrolyte weight uptake vs. time for pristine and 250 °C treated electrodes: (b) LTO, (c) TiO_2, and (d) graphite.

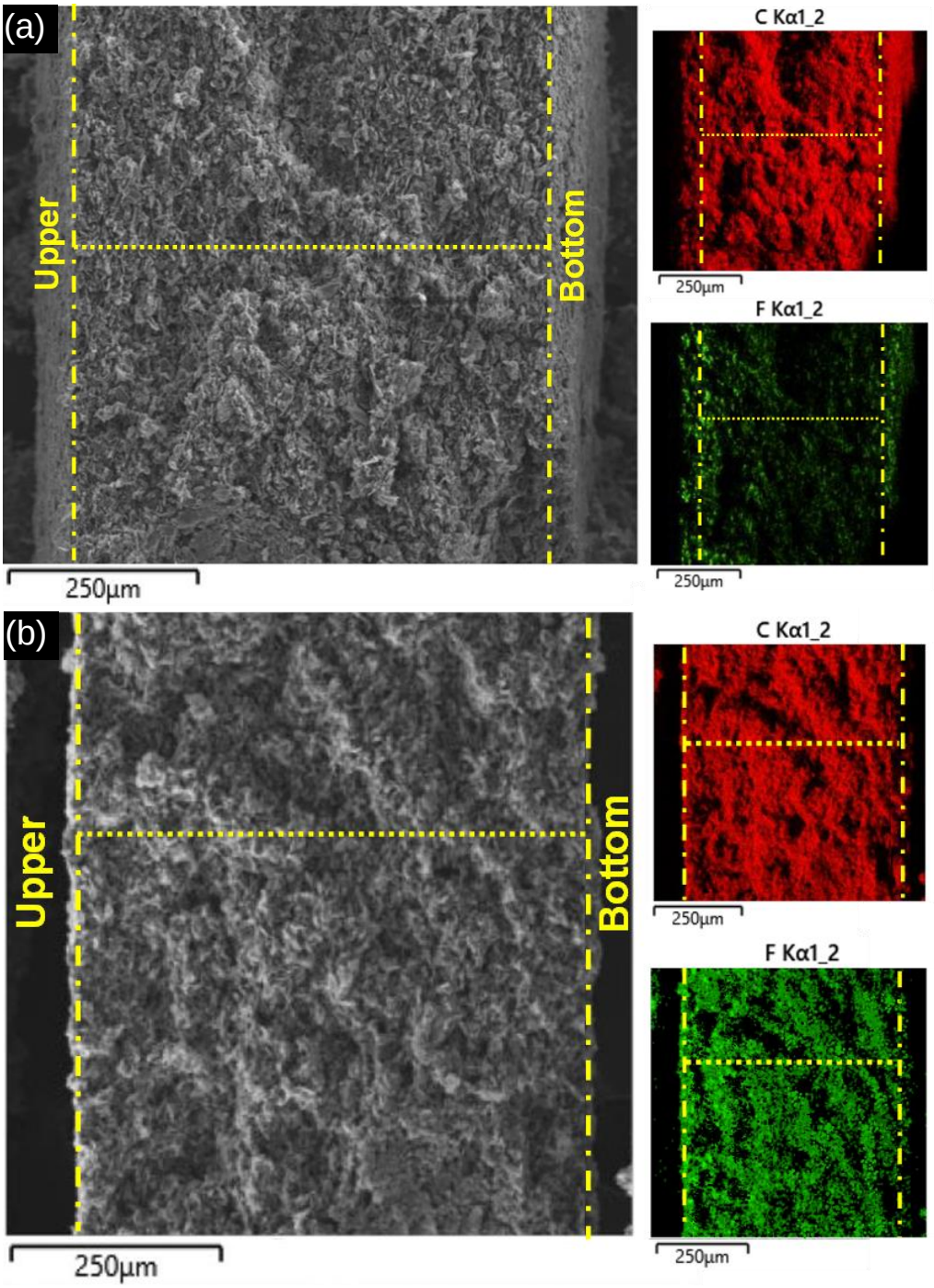

Figure S5. SEM images and EDS mapping of the cross-sectional area of (a) pristine graphite electrode and (b) 250 °C treated graphite electrode.

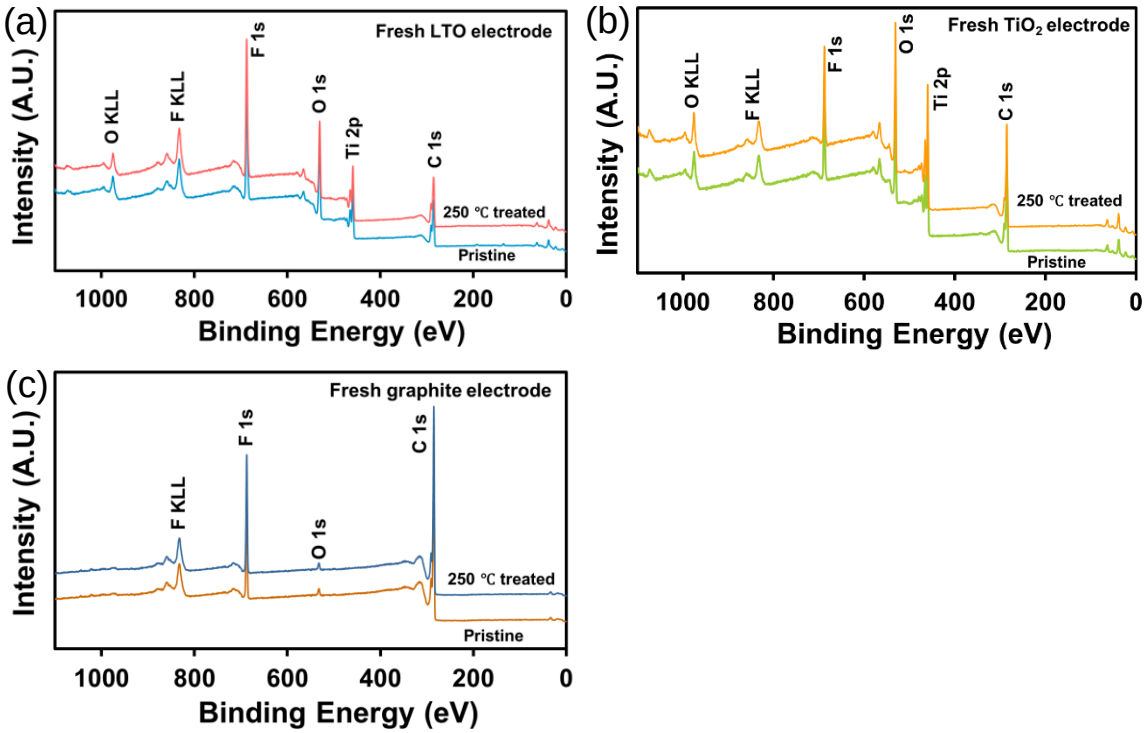

Figure S6. XPS survey spectra of fresh electrodes: (a) LTO, (b) TiO_2, and (c) graphite.

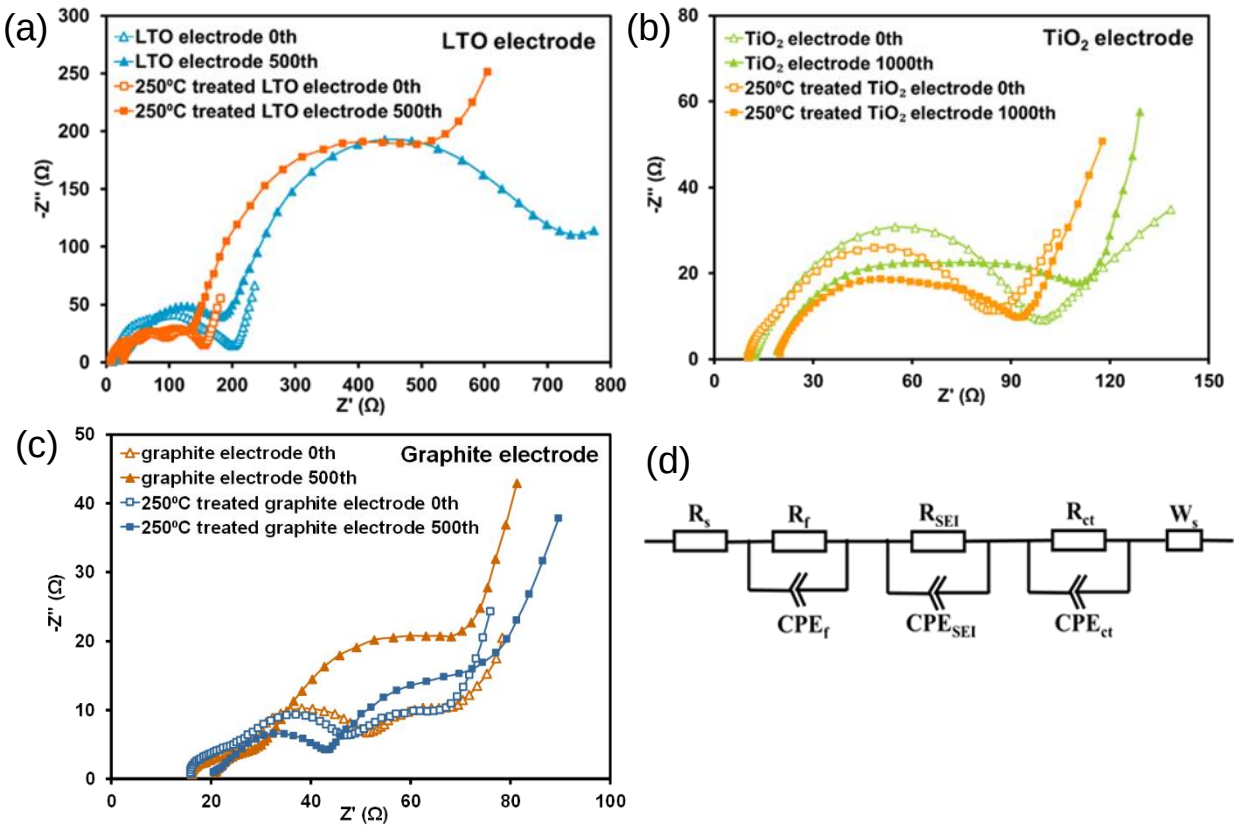

Figure S7. Nyquist plots of (a) LTO, (b) TiO_2, and (c) graphite electrodes tested at a 1 C rate with a potential range of 0.1 V – 3.0 V at 0^{th} (after the formation at a 0.1 C rate for 3 cycles) and after long-term cycling. (d) Equivalent circuit.

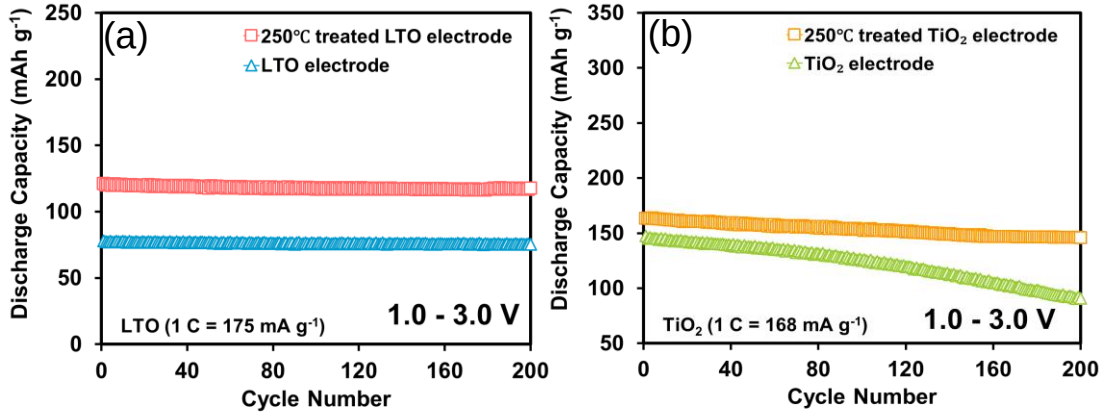

Figure S8. Cycling performance of (a) LTO and (b) TiO_2 with and without 250 °C treatment within a potential range of 1.0 – 3.0 V.

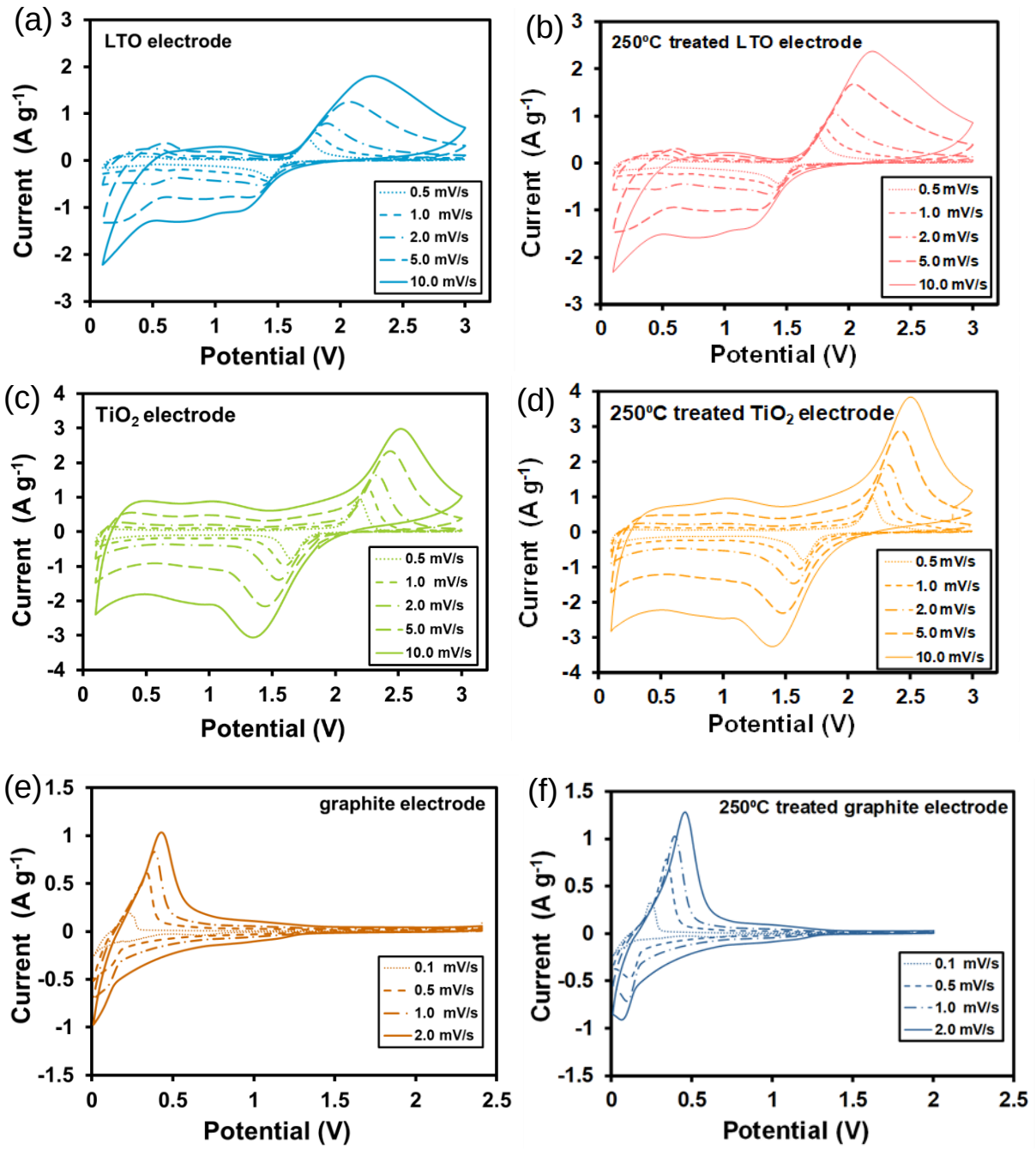

Figure S9. CV curves of (a) pristine LTO, (b) 250 °C treated LTO, (c) pristine TiO_2, and (d) 250 °C treated TiO_2 electrodes at different scan rates of 0.5, 1.0, 2.0, 5.0, and 10.0 mV s^{-1}. CV curves of (e) pristine graphite and (f) 250 °C treated graphite electrodes at different scan rates of 0.1, 0.5, 1.0, and 2.0 mV s^{-1}.

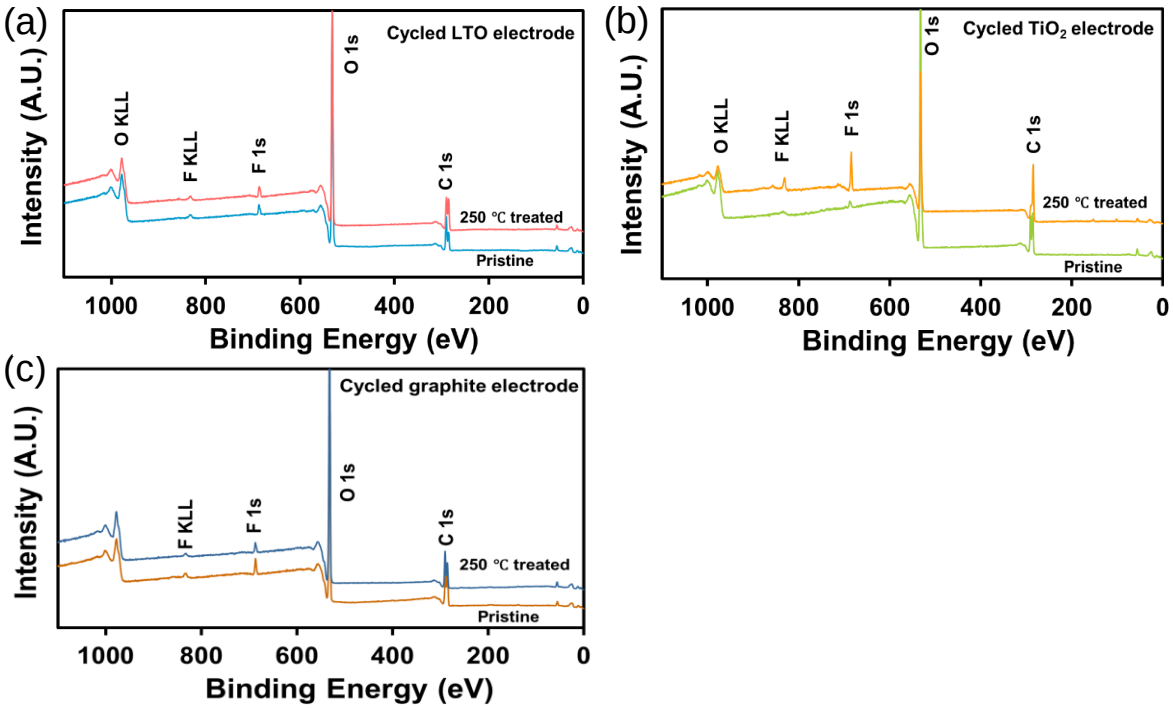

Figure S10. XPS survey spectra of electrodes: (a) LTO after 500 cycles of charge/discharge, (b) TiO_2 after 1,000 cycles of charge/discharge, and (c) graphite after 500 cycles of charge/discharge.

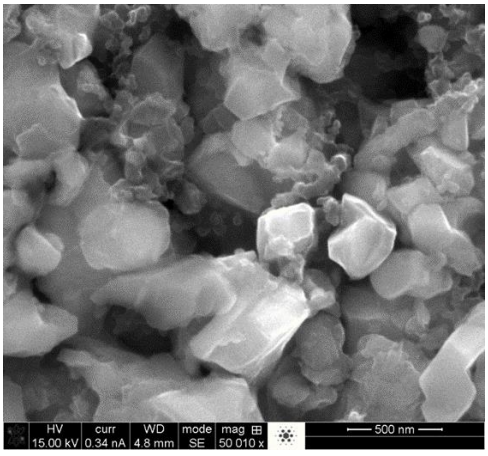

Figure S11. SEM image of fresh LTO electrode without 250 °C treatment.

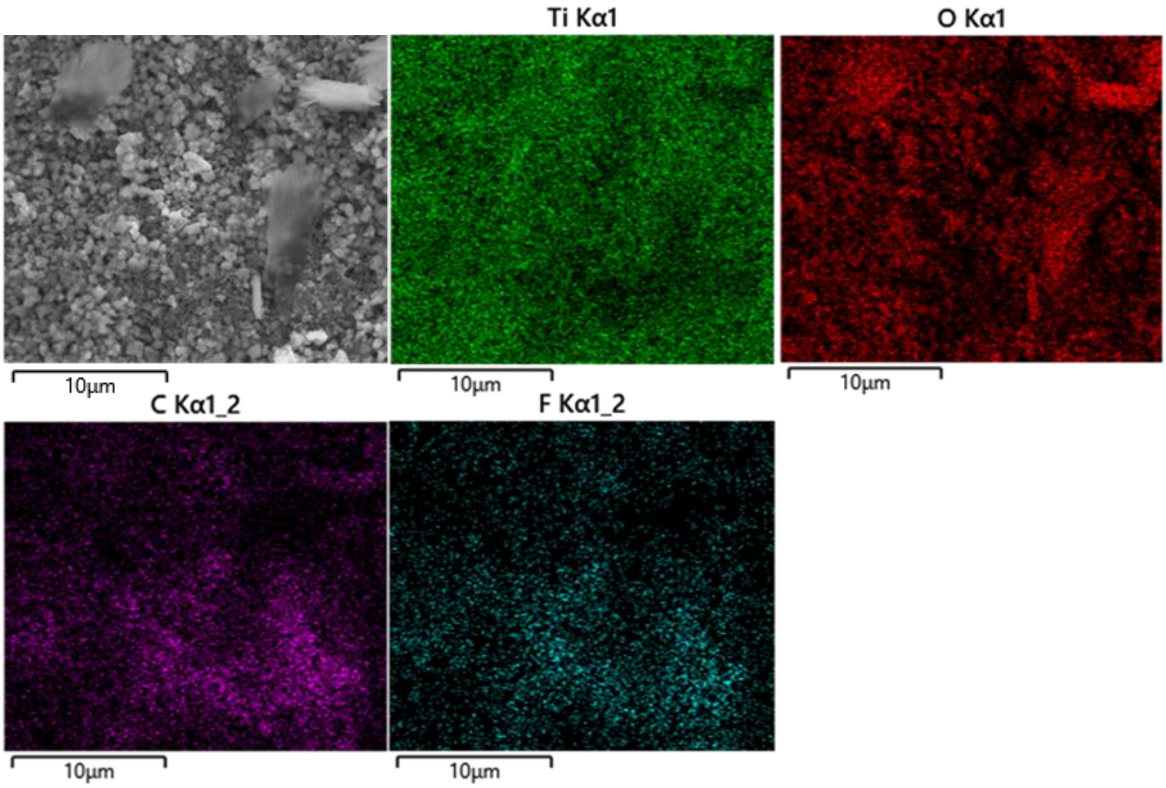

Figure S12. SEM image and EDS mapping of pristine LTO electrode after 500 cycles of charge/discharge.

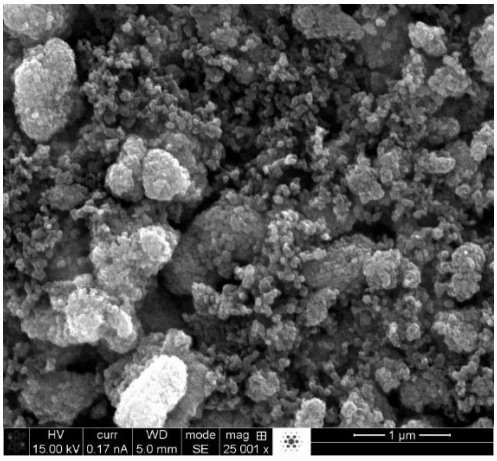

Figure S13. SEM image of fresh TiO_2 electrode with 250 °C treatment.

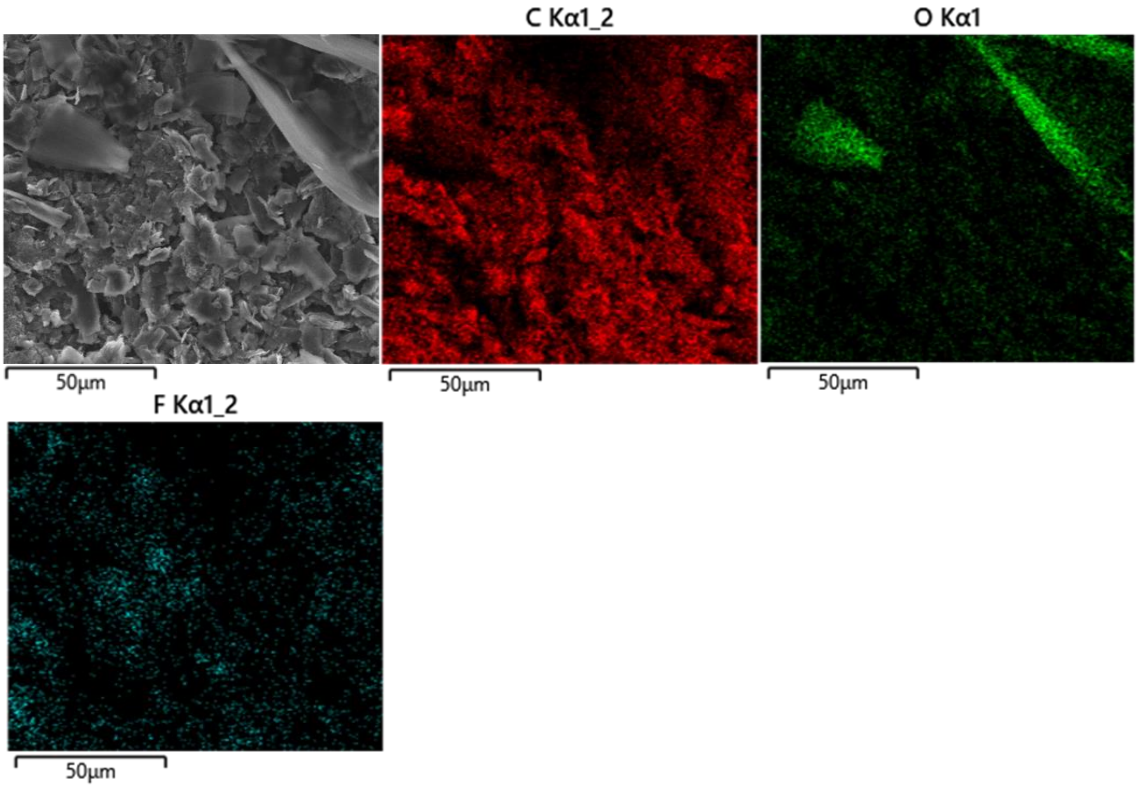

Figure S14. SEM image and EDS mapping of pristine graphite electrode after 500 cycles of charge/discharge.

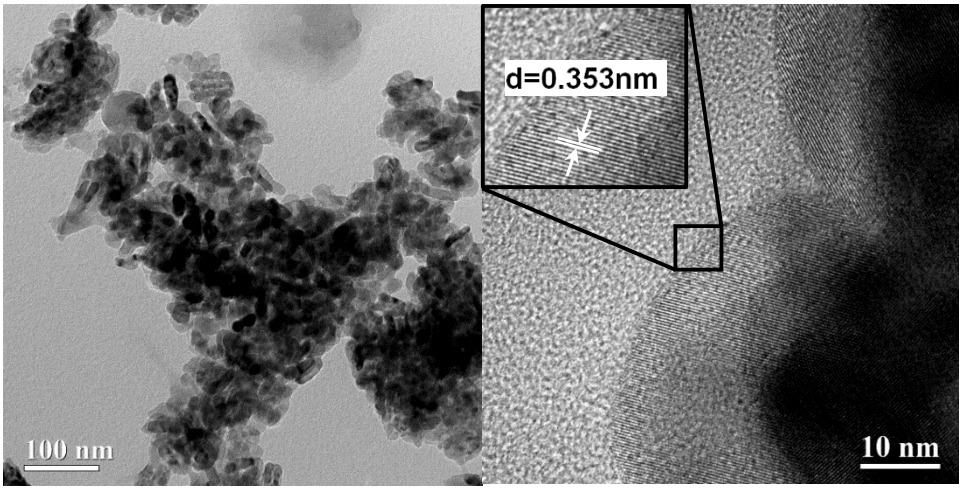

Figure S15. TEM images of pure TiO_2 nanoparticles.