Supporting Information for

Structural and electrochemical characteristics of Ca-doped 'flower-like' $Li_4Ti_5O_{12}$ motifs as high-rate anode materials for lithium-ion batteries

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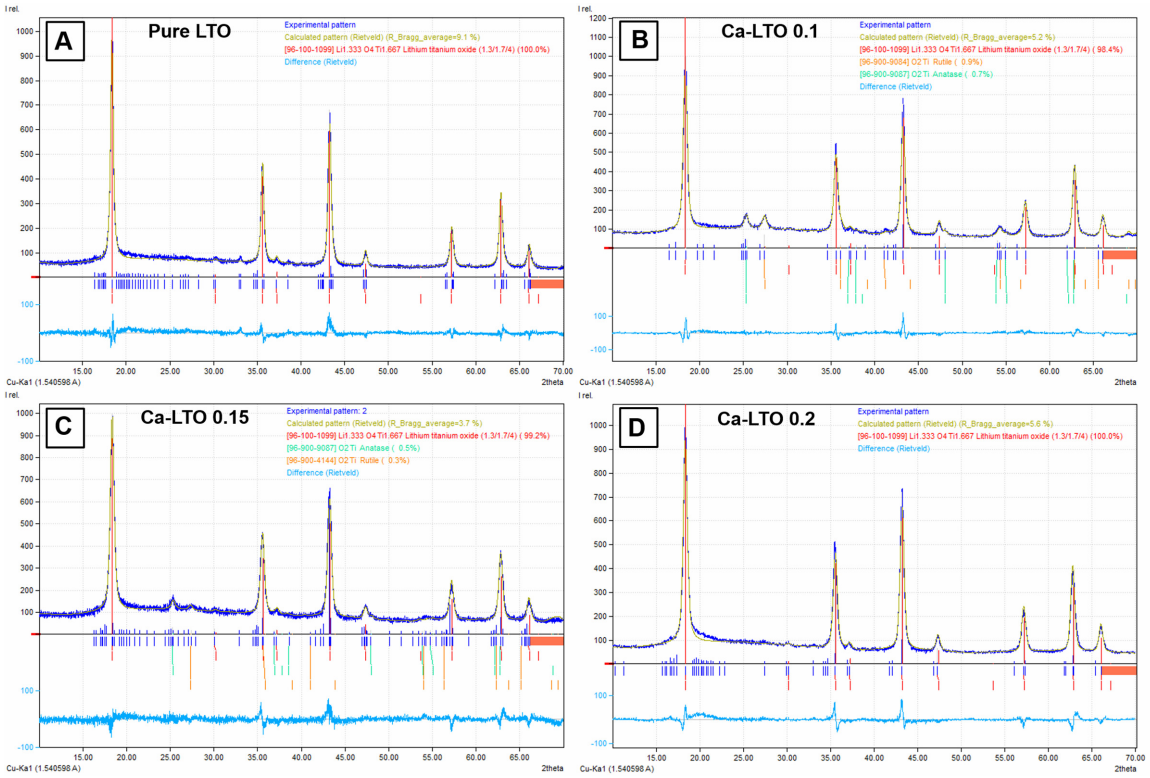

Figure S1. Rietveld refinement results associated with the X-ray diffraction patterns of (A) undoped LTO as well as of the corresponding Ca-doped LTO samples: (B) 'x' = 0.1, (C) 'x' = 0.15, and (D) 'x' = 0.2.

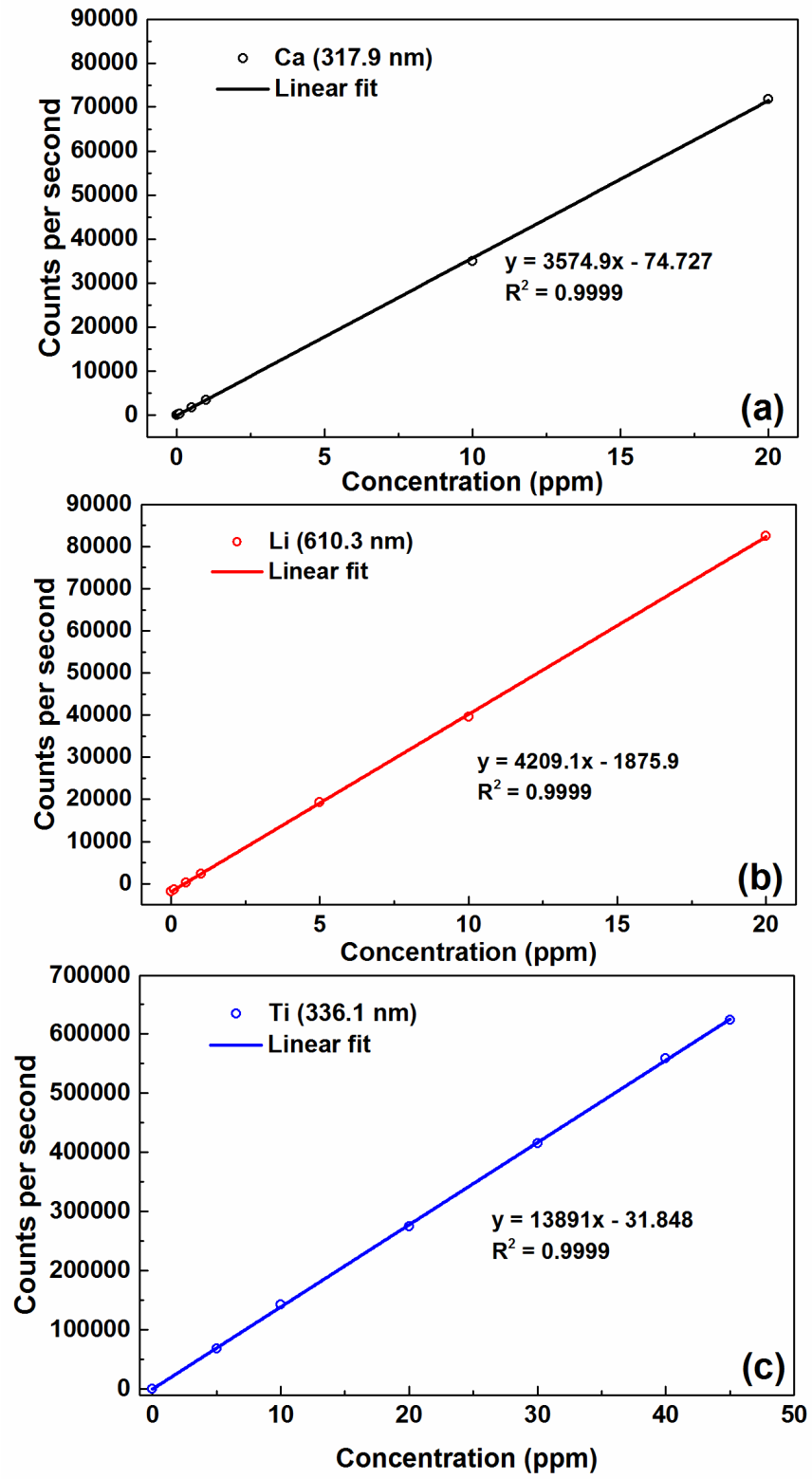

Figure S2. Calibration curves corresponding to the presence of (**a**) Ca, (**b**) Li, and (**c**) Ti elements, detected in the ICP-OES measurement.

Table S1. Atomic positions of the Ca-doped LTO structure, after refinement using the cubic *Fd-3m* structure .

label	elem	mult	x	y	z	frac
Li1	Li+1	8	0.125	0.125	0.125	1
Li2	Li+1	16	0.5	0.5	0.5	0.13(1)
Ti1	Ti+4	16	0.5	0.5	0.5	0.8333
O1	O-2	32	0.26246	0.26246	0.26246	1
Ca5	Ca+2	16	0.5	0.5	0.5	0.03(1)

Table S2. Cell parameters after structural refinement using the DFT calculated model.

Space Group:	*P* 1					
a	***b***	***c***	**alpha**	**beta**	**gamma**	**volume**
11.81(2)	11.83(2)	14.49(1)	89.9(3)	89.9(3)	119.9(1)	1755.4(2)

Table S3. Atomic positions for the Ca-doped LTO structure after refinement using the DFT calculated model.

label	element	mult	x	y	z	frac
Li1	Li	1	0.247776	0.252224	0.878723	1
Li2	Li	1	0.252224	0.247776	0.121287	1
Li3	Li	1	0.413632	0.086368	0.203766	1
Ca4	Ca+2	1	0.086368	0.413632	0.796243	1
Li4	Li	1	0.417116	0.082884	0.45178	1
Li5	Li	1	0.082885	0.417115	0.54822	1
Li6	Li	1	0.25	0.25	0.500001	1
Li7	Li	1	0	0	0.000001	1
Li8	Li	1	0.747776	0.252224	0.878723	1
Li9	Li	1	0.752224	0.247776	0.121287	1
Li10	Li	1	0.913632	0.086368	0.203766	1
Li11	Li	1	0.586368	0.413632	0.796243	1
Li12	Li	1	0.917116	0.082884	0.45178	1
Li13	Li	1	0.582885	0.417115	0.54822	1
Li14	Li	1	0.75	0.25	0.500001	1
Li15	Li	1	0.5	0	0.000001	1
Li16	Li	1	0.247776	0.752224	0.878723	1
Li17	Li	1	0.252224	0.747776	0.121287	1
Li18	Li	1	0.413632	0.586368	0.203766	1
Li19	Li	1	0.086368	0.913632	0.796243	1
Li20	Li	1	0.417116	0.582884	0.45178	1
Li21	Li	1	0.082885	0.917115	0.54822	1
Li22	Li	1	0.25	0.75	0.500001	1
Li23	Li	1	0	0.5	0.000001	1
Li24	Li	1	0.747776	0.752224	0.878723	1
Li25	Li	1	0.752224	0.747776	0.121287	1
Li26	Li	1	0.913632	0.586368	0.203766	1
Li27	Li	1	0.586368	0.913632	0.796243	1
Li28	Li	1	0.917116	0.582884	0.45178	1
Li29	Li	1	0.582885	0.917115	0.54822	1
Li30	Li	1	0.75	0.75	0.500001	1
Li31	Li	1	0.5	0.5	0.000001	1
Ti1	Ti	1	0.25	0	0.000003	1
Ti2	Ti	1	0	0.25	0	1
Ti3	Ti	1	0.08589	0.167965	0.66245	1
Ti4	Ti	1	0.167961	0.085886	0.337552	1
Ti5	Ti	1	0.414114	0.332039	0.337552	1
Ti6	Ti	1	0.332035	0.41411	0.66245	1
Ti7	Ti	1	0.332686	0.167314	0.66411	1

Ti8	Ti	1	0.167313	0.332687	0.335886	1
Ti9	Ti	1	0.421462	0.078538	0.838452	1
Ti10	Ti	1	0.078537	0.421463	0.161554	1
Ti11	Ti	1	0.75	0	0.000003	1
Ti12	Ti	1	0.5	0.25	0.000003	1
Ti13	Ti	1	0.58589	0.167965	0.66245	1
Ti14	Ti	1	0.667961	0.085886	0.337552	1
Ti15	Ti	1	0.914114	0.332039	0.337552	1
Ti16	Ti	1	0.832035	0.41411	0.66245	1
Ti17	Ti	1	0.832686	0.167314	0.66411	1
Ti18	Ti	1	0.667313	0.332687	0.335886	1
Ti19	Ti	1	0.921462	0.078538	0.838452	1
Ti20	Ti	1	0.578537	0.421463	0.161554	1
Ti21	Ti	1	0.25	0.5	0.000003	1
Ti22	Ti	1	0	0.75	0.000003	1
Ti23	Ti	1	0.08589	0.667965	0.66245	1
Ti24	Ti	1	0.167961	0.585886	0.337552	1
Ti25	Ti	1	0.414114	0.832039	0.337552	1
Ti26	Ti	1	0.332035	0.91411	0.66245	1
Ti27	Ti	1	0.332686	0.667314	0.66411	1
Ti28	Ti	1	0.167313	0.832687	0.335886	1
Ti29	Ti	1	0.421462	0.578538	0.838452	1
Ti30	Ti	1	0.078537	0.921463	0.161554	1
Ti31	Ti	1	0.75	0.5	0.000003	1
Ti32	Ti	1	0.5	0.75	0.000003	1
Ti33	Ti	1	0.58589	0.667965	0.66245	1
Ti34	Ti	1	0.667961	0.585886	0.337552	1
Ti35	Ti	1	0.914114	0.832039	0.337552	1
Ti36	Ti	1	0.832035	0.91411	0.66245	1
Ti37	Ti	1	0.832686	0.667314	0.66411	1
Ti38	Ti	1	0.667313	0.832687	0.335886	1
Ti39	Ti	1	0.921462	0.578538	0.838452	1
Ti40	Ti	1	0.578537	0.921463	0.161554	1
O1	O	1	0.249845	0.250155	0.262581	1
O2	O	1	0.250156	0.249844	0.737423	1
O3	O	1	0.433835	0.333985	0.084588	1
O4	O	1	0.333988	0.433837	0.915417	1
O5	O	1	0.066163	0.166012	0.915417	1
O6	O	1	0.166015	0.066165	0.084588	1
O7	O	1	0.158816	0.341184	0.081632	1
O8	O	1	0.341184	0.158816	0.918367	1
O9	O	1	0.404851	0.327412	0.595405	1
O10	O	1	0.327412	0.404852	0.404597	1

O11	O	1	0.095148	0.172588	0.404597	1
O12	O	1	0.172588	0.095149	0.595405	1
O13	O	1	0.172516	0.327484	0.594844	1
O14	O	1	0.327485	0.172515	0.405159	1
O15	O	1	0.417023	0.082977	0.59276	1
O16	O	1	0.082977	0.417023	0.407247	1
O17	O	1	0.270253	0.009364	0.743054	1
O18	O	1	0.009365	0.270253	0.25695	1
O19	O	1	0.229747	0.490635	0.25695	1
O20	O	1	0.490636	0.229747	0.743054	1
O21	O	1	0.411458	0.088542	0.069512	1
O22	O	1	0.088541	0.411459	0.930488	1
O23	O	1	0.49186	0.00814	0.744659	1
O24	O	1	0.00814	0.49186	0.255345	1
O25	O	1	0.749845	0.250155	0.262581	1
O26	O	1	0.750156	0.249844	0.737423	1
O27	O	1	0.933835	0.333985	0.084588	1
O28	O	1	0.833988	0.433837	0.915417	1
O29	O	1	0.566163	0.166012	0.915417	1
O30	O	1	0.666015	0.066165	0.084588	1
O31	O	1	0.658816	0.341184	0.081632	1
O32	O	1	0.841184	0.158816	0.918367	1
O33	O	1	0.904851	0.327412	0.595405	1
O34	O	1	0.827412	0.404852	0.404597	1
O35	O	1	0.595148	0.172588	0.404597	1
O36	O	1	0.672588	0.095149	0.595405	1
O37	O	1	0.672516	0.327484	0.594844	1
O38	O	1	0.827485	0.172515	0.405159	1
O39	O	1	0.917023	0.082977	0.59276	1
O40	O	1	0.582977	0.417023	0.407247	1
O41	O	1	0.770253	0.009364	0.743054	1
O42	O	1	0.509365	0.270253	0.25695	1
O43	O	1	0.729747	0.490635	0.25695	1
O44	O	1	0.990636	0.229747	0.743054	1
O45	O	1	0.911458	0.088542	0.069512	1
O46	O	1	0.588541	0.411459	0.930488	1
O47	O	1	0.99186	0.00814	0.744659	1
O48	O	1	0.50814	0.49186	0.255345	1
O49	O	1	0.249845	0.750155	0.262581	1
O50	O	1	0.250156	0.749844	0.737423	1
O51	O	1	0.433835	0.833985	0.084588	1
O52	O	1	0.333988	0.933837	0.915417	1
O53	O	1	0.066163	0.666012	0.915417	1

O54	O	1	0.166015	0.566165	0.084588	1
O55	O	1	0.158816	0.841184	0.081632	1
O56	O	1	0.341184	0.658816	0.918367	1
O57	O	1	0.404851	0.827412	0.595405	1
O58	O	1	0.327412	0.904852	0.404597	1
O59	O	1	0.095148	0.672588	0.404597	1
O60	O	1	0.172588	0.595149	0.595405	1
O61	O	1	0.172516	0.827484	0.594844	1
O62	O	1	0.327485	0.672515	0.405159	1
O63	O	1	0.417023	0.582977	0.59276	1
O64	O	1	0.082977	0.917023	0.407247	1
O65	O	1	0.270253	0.509364	0.743054	1
O66	O	1	0.009365	0.770253	0.25695	1
O67	O	1	0.229747	0.990635	0.25695	1
O68	O	1	0.490636	0.729747	0.743054	1
O69	O	1	0.411458	0.588542	0.069512	1
O70	O	1	0.088541	0.911459	0.930488	1
O71	O	1	0.49186	0.50814	0.744659	1
O72	O	1	0.00814	0.99186	0.255345	1
O73	O	1	0.749845	0.750155	0.262581	1
O74	O	1	0.750156	0.749844	0.737423	1
O75	O	1	0.933835	0.833985	0.084588	1
O76	O	1	0.833988	0.933837	0.915417	1
O77	O	1	0.566163	0.666012	0.915417	1
O78	O	1	0.666015	0.566165	0.084588	1
O79	O	1	0.658816	0.841184	0.081632	1
O80	O	1	0.841184	0.658816	0.918367	1
O81	O	1	0.904851	0.827412	0.595405	1
O82	O	1	0.827412	0.904852	0.404597	1
O83	O	1	0.595148	0.672588	0.404597	1
O84	O	1	0.672588	0.595149	0.595405	1
O85	O	1	0.672516	0.827484	0.594844	1
O86	O	1	0.827485	0.672515	0.405159	1
O87	O	1	0.917023	0.582977	0.59276	1
O88	O	1	0.582977	0.917023	0.407247	1
O89	O	1	0.770253	0.509364	0.743054	1
O90	O	1	0.509365	0.770253	0.25695	1
O91	O	1	0.729747	0.990635	0.25695	1
O92	O	1	0.990636	0.729747	0.743054	1
O93	O	1	0.911458	0.588542	0.069512	1
O94	O	1	0.588541	0.911459	0.930488	1
O95	O	1	0.99186	0.50814	0.744659	1
O96	O	1	0.50814	0.99186	0.255345	1

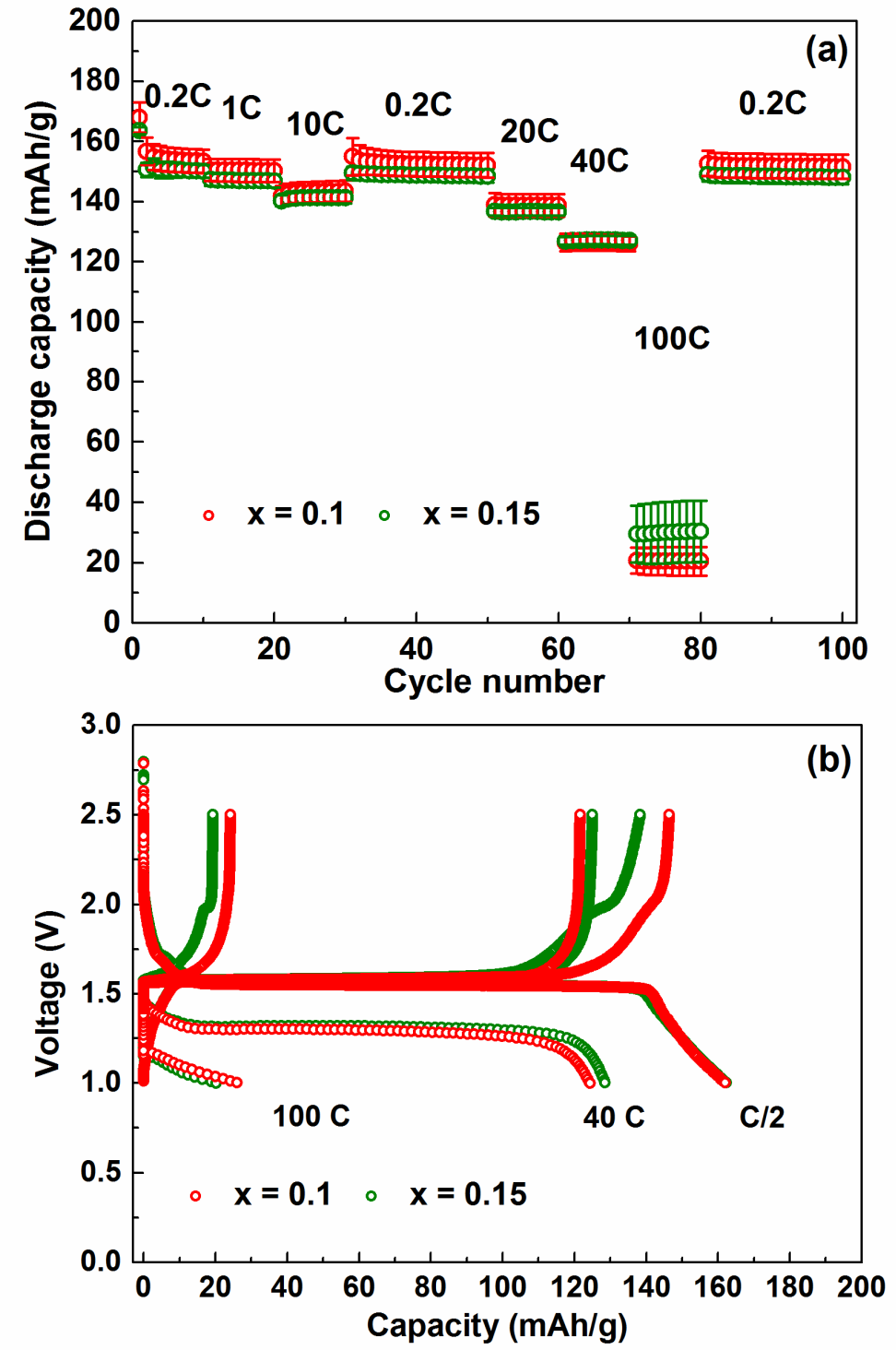

Figure S3. (a) Capacity values measured under a series of discharge rates for Ca-doped $Li_{4-x}Ca_xTi_5O_{12}$ ('x' = 0.1 and 0.15) based electrodes, respectively. (b) Discharge and charge curves at C/2 (cycle 1), 40C (cycle 70), and 100C rates (cycle 80) for Ca-doped $Li_{4-x}Ca_xTi_5O_{12}$ ('x' = 0.1 and 0.15) 3D 'flower-like' LTO electrodes.

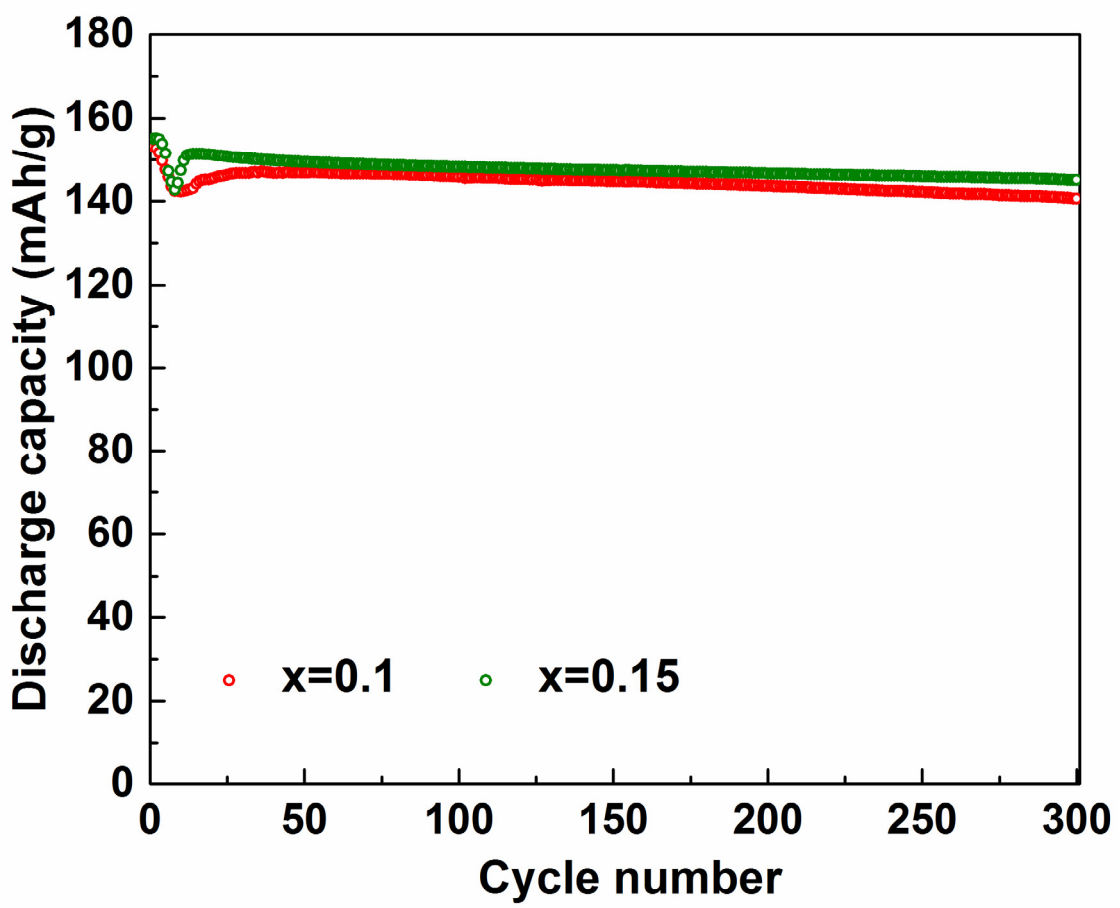

Figure S4. The cycling performance of Ca-doped $Li_{4-x}Ca_xTi_5O_{12}$ ('x' = 0.1 and 0.15) based electrodes at a 20C discharge rate.

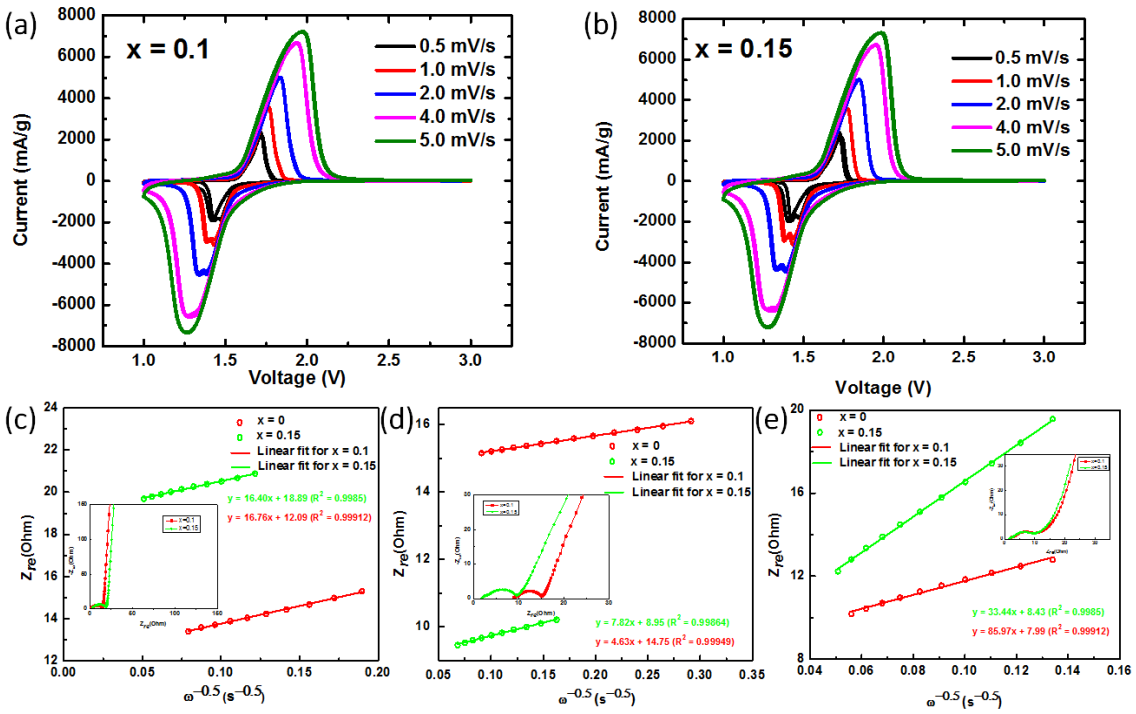

Figure S5. Cyclic voltammetry curves for (a) 'x' = 0.1 and (b) 'x'= 0.15 Ca-doped $Li_{4-x}Ca_xTi_5O_{12}$ based electrodes as a function of the scan rate from 0.5 to 5.0 mV/s; (c-e) Linear fit of the Warburg region from AC impedance with the inset of the Nyquist plot for Ca-doped $Li_{4-x}Ca_xTi_5O_{12}$ ('x' = 0.1 and 0.15) electrode (c) before cycling, (d) after full lithiation, and (e) after full de-lithiation in cycle 50.

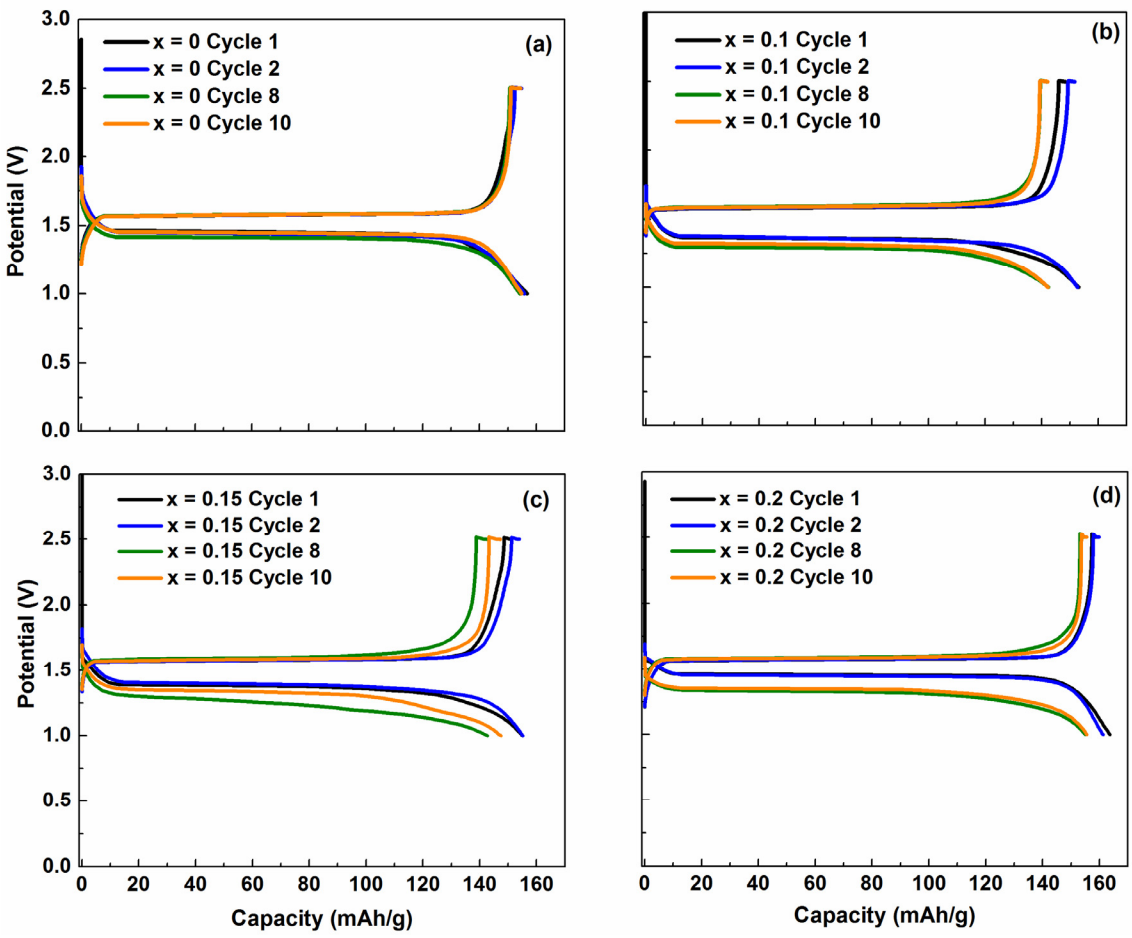

Figure S6. Discharge and charge curves at cycles 1, 2, 8, and 10 for 'x' = 0, 0.1, 0.15, and 0.2 Ca-doped LTO electrodes.

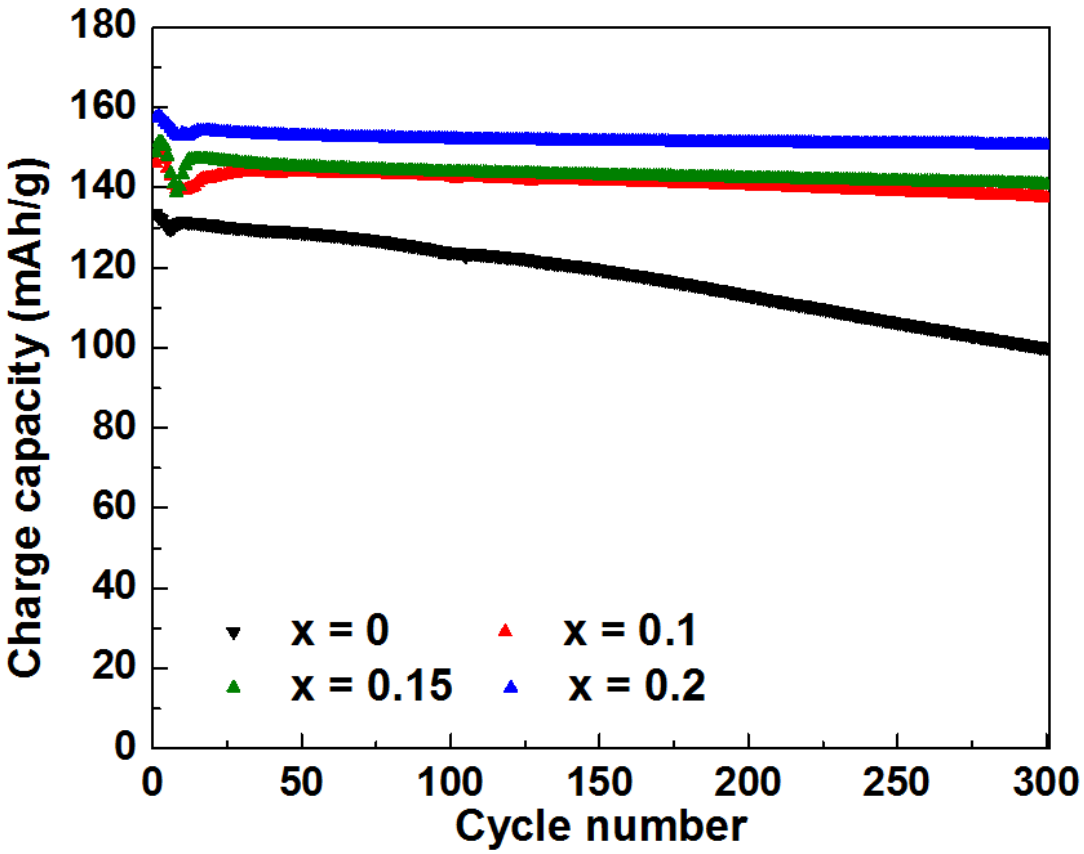

Figure S7. Charge capacity versus cycle number for 'x' = 0, 0.1, 0.15, and 0.2 Ca-doped LTO samples at a 1C charge rate.

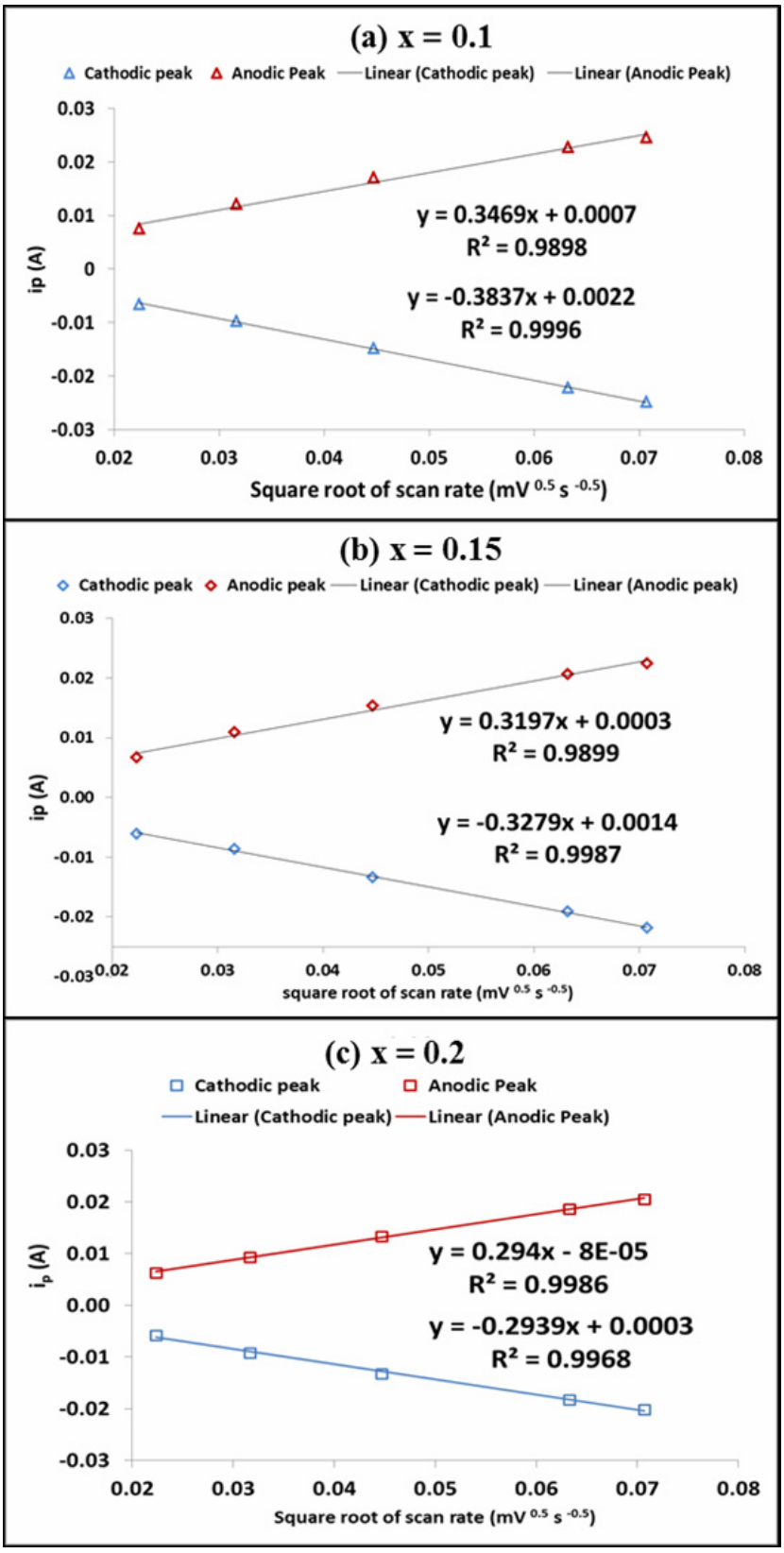

Figure S8. Linear fit of the peak current (i_p) as a function of scan rate square root for (a) 'x' = 0.1, (b) 'x' = 0.15, and (c) 'x' = 0.2 Ca-doped $Li_{4-x}Ca_xTi_5O_{12}$ electrodes.

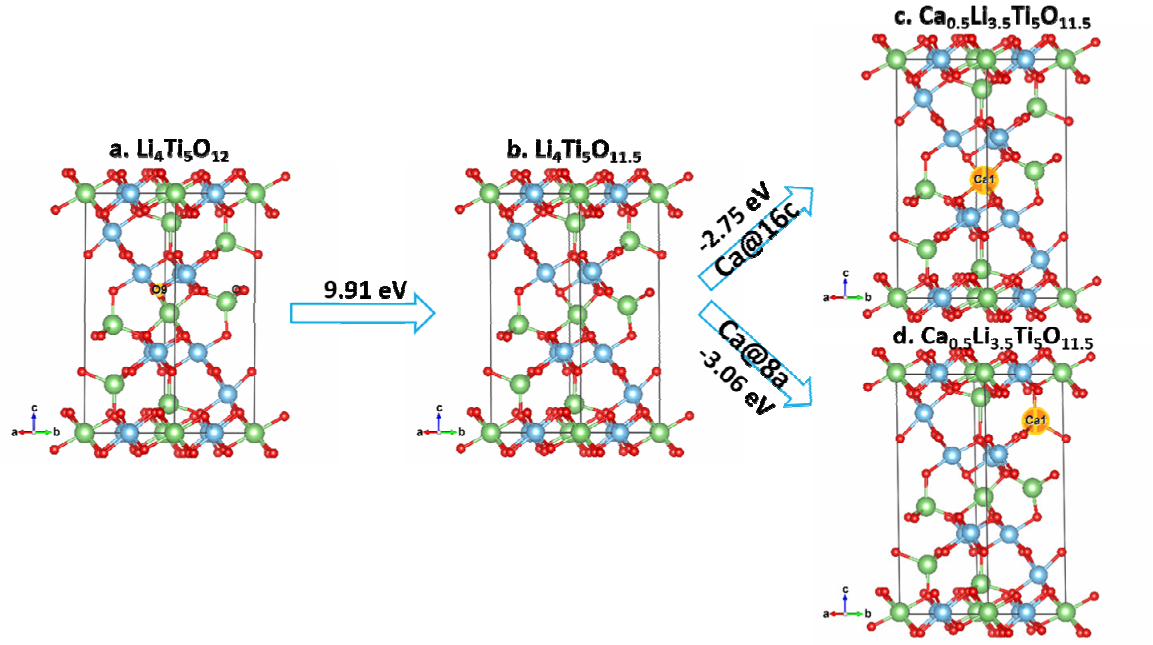

Figure S9. Structures and associated energies for generation of oxygen vacancies: (**a**) $Li_4Ti_5O_{12}$ → (**b**) $Li_4Ti_5O_{11.5}$ and doping of Ca^{2+} ions at (**c**) 16 c and (**d**) 8a sites of $Li_4Ti_5O_{12}$ (orange: Ca; green: Li; blue: Ti; red: O).

Table S4. R_{ct} as well as D_{Li+} for each electrode, including data for both undoped and Ca-doped materials, using the circuit shown below the table. Circuit A was used to fit the electrodes before cycling, while circuit B was used to fit the electrodes in cycle 50, both after lithiation and de-lithiation.

Active material	Condition	R_{ct} (Ohm)	D_{Li+} (cm^2s^{-1})
$Li_4Ti_5O_{12}$ ('x' = 0)	Before cycling	22.4	$6.2 \cdot 10^{-12}$
	After lithiation (cycle 50)	5.9	$6.1 \cdot 10^{-11}$
	After de-lithiation (cycle 50)	15.7	$1.5 \cdot 10^{-12}$
$Li_{4-x}Ca_xTi_5O_{12}$ ('x' = 0.1)	Before cycling	12.5	$2.8 \cdot 10^{-12}$
	After lithiation (cycle 50)	5.6	$5.2 \cdot 10^{-11}$
	After de-lithiation (cycle 50)	6.8	$9.7 \cdot 10^{-13}$
$Li_{4-x}Ca_xTi_5O_{12}$ ('x' = 0.15)	Before cycling	17.7	$4.2 \cdot 10^{-12}$
	After lithiation (cycle 50)	6.8	$2.8 \cdot 10^{-11}$
	After de-lithiation (cycle 50)	6.2	$1.1 \cdot 10^{-13}$
$Li_{4-x}Ca_xTi_5O_{12}$ ('x' = 0.2)	Before cycling	11.9	$3.2 \cdot 10^{-12}$
	After lithiation (cycle 50)	5.5	$4.1 \cdot 10^{-11}$
	After de-lithiation (cycle 50)	5.3	$4.6 \cdot 10^{-13}$

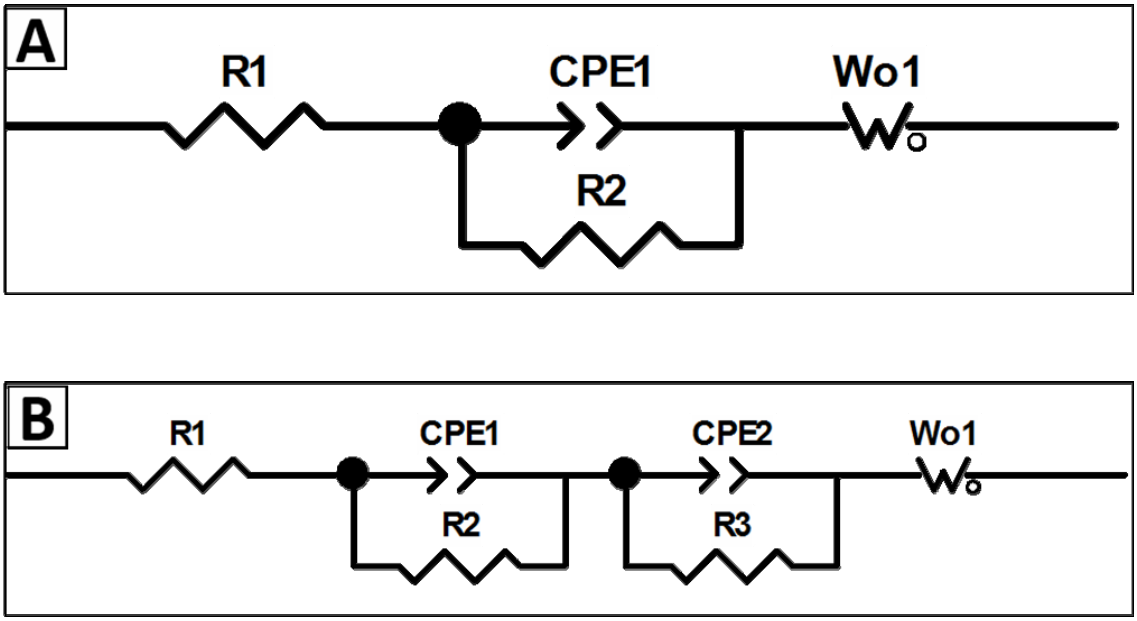

Figure S10. The equivalent electrical circuits used to fit the impedance spectra of the cells both (**A**) before and (**B**) after cycling.