Supplementary Information (SI) for EES Batteries.

Supplementary Information: Chemo-Mechanical Deformations in Lithium Titanate Composite Electrode Upon Over Lithiation

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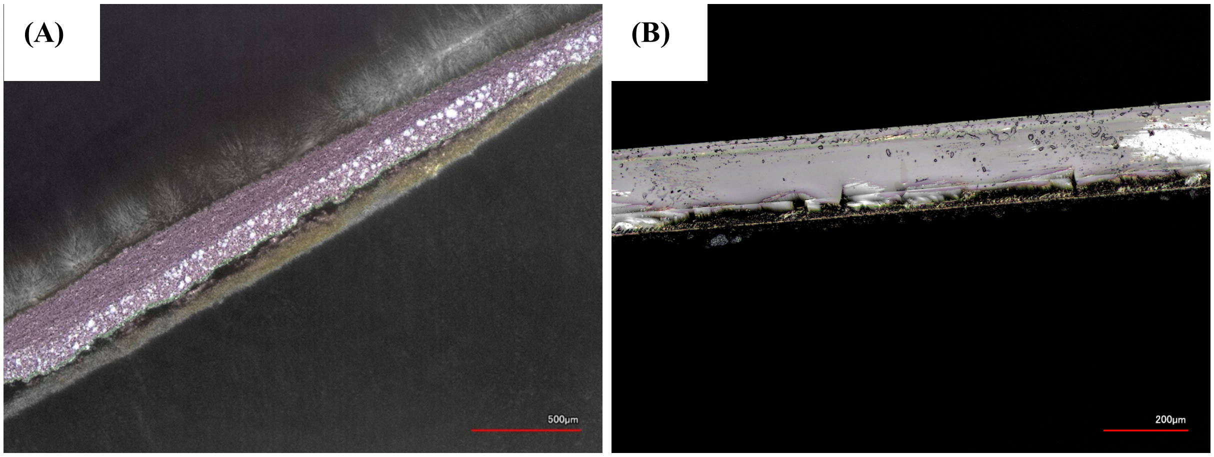
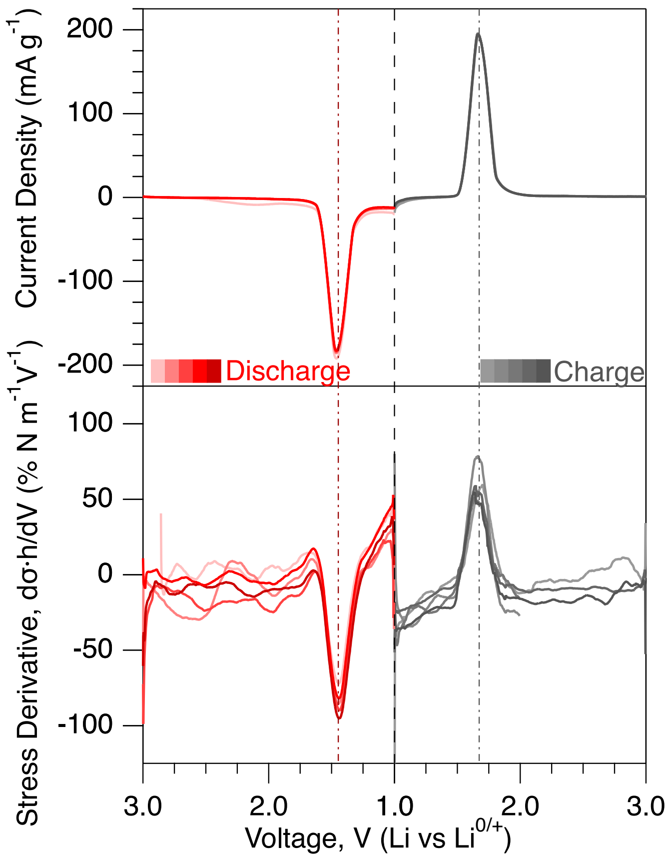
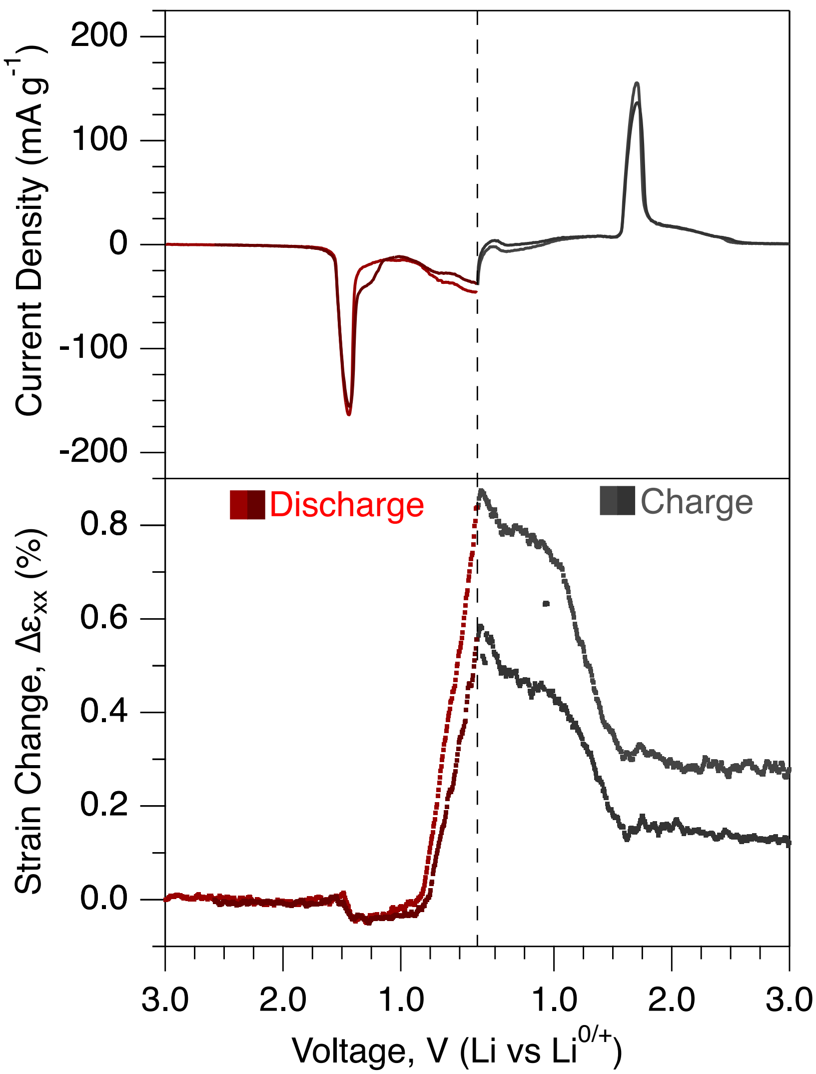


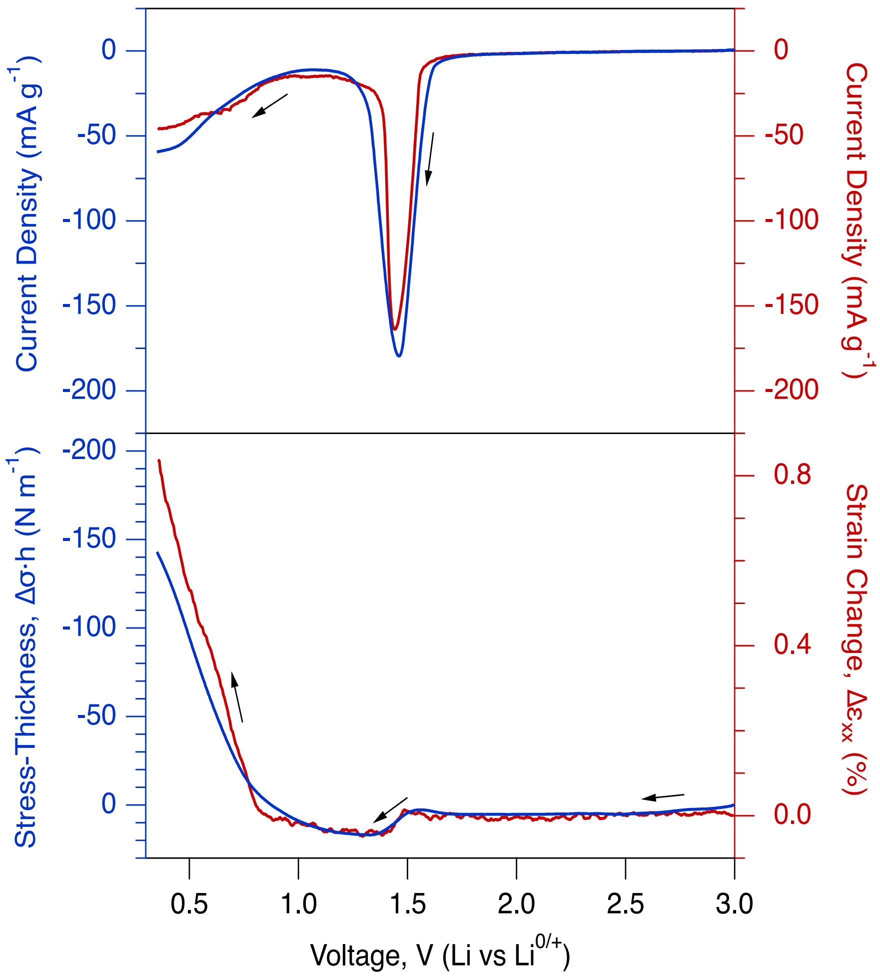
Supp. Figure 1: Optical image of (A) the pristine free-standing composite electrode for strain measurements and (B) composite electrode on silicon substrate for stress measurement.



Supp. Figure 2: Evolution of stress derivative during discharge and charge during the initial five cycles.



Supp. Figure 3: Strain changes during sixth and seventh cycles between 0.35 – 3.0 V (vs $Li/Li^{0/+}$). Strains were set to zero at the beginning of each discharge for better comparison.



Supp. Figure 4: Stress and strain generation from Figure 3A and C was plotted in the same plot for better demonstration.

Strain Calculations in Composite Electrode

The volumetric expansions in the composite electrode were predicted based on unit lattice distortion in the electrode's structure, and by adopting the inverse rule of mixtures and open-cell theory. Table 1 shows the properties of the lithium titanate electrode, Super P conductive carbon, and CMC binder in the model. Table 2 lists the governing equations, including the inverse rule of mixtures, open-cell theory, S-Combining Rule, and linear strain calculations. [1–4] Tables 3 and 4 demonstrate the nomenclatures used in the following equations and the list of variables with their descriptions, respectively. The density of the free-standing composite LTO electrode from strain measurements was measured to be around 1.45 g/cm^3. The porosity of the free-standing composite electrode was estimated to be 0.485% (equation 10). The details of the model were also previously explained in detail in our previous publication. [5]

Table 1: Material Properties of the Composite Electrode Matrix [1,6,7]

Material Properties of the Composite Electrode Matrix				
Material	Fraction of Total Mass	Density (g/cm^3)	Elastic Modulus (GPa)	Poisson's Ratio
Li4Ti5O12	0.8	3.50	152	0.27
CMC binder	0.1	1.6	1.2	0.45
Super P Carbon	0.1	1.9	32.47	0.315

Table 2: The list of equations in the model [1–4]

$$\frac{1}{K_m} = \frac{\phi_{m,cc}}{K_{cc}} + \frac{\phi_{m,cmc}}{K_{cmc}}$$	(1)
$$\frac{1}{G_m} = \frac{\phi_{m,cc}}{G_{cc}} + \frac{\phi_{m,cmc}}{G_{cmc}}$$	(2)
$$\phi_{m,cmc} = \frac{\phi_{cmc}}{\phi_{cmc} + \phi_{cc}}$$	(3)
$$\phi_{m,cb} = \frac{\phi_{cc}}{\phi_{cmc} + \phi_{cc}}$$	(4)
$$K_{pm} = \left(\frac{1}{3(1-2\nu_{pm})}\right)\left(\frac{K_m G_m}{3K_m + G_m}\right)\left(\frac{\rho_{pm}}{\rho_m}\right)^2$$	(5)
$$\rho_m = \phi_{m,cc}\rho_{cc} + \phi_{m,cmc}\rho_{cmc}$$	(6)
$$\rho_{pm} = \phi_{pm,cc}\rho_{cc} + \phi_{pm,cmc}\rho_{cmc}$$	(7)
$$\phi_{pm,cmc} = \frac{\phi_{cmc}}{\phi_{pm}}$$	(8)

$$\phi_{pm,cb} = \frac{\phi_{cc}}{\phi_{pm}}$$	(9)
$$\phi_{pm} = \phi_{cc} + \phi_{cmc} + \phi_p = 1 - \phi_{LTO}$$	(10)
$$K_{ce} = \frac{K_{pm}(1 + \phi_{LTO}\xi_l\chi)}{1 - \phi_{LTO}\Psi\chi}$$	(11)
$$\chi = \frac{K_{LTO} - K_{pm}}{K_{LTO} - \xi_l K_{pm}}$$	(12)
$$\Psi = 1 + \frac{\phi_{LTO}\phi_{pm}(1 - \gamma\phi_{pm})(K_{LTO} - K_{pm})\left(\frac{2(1 - 2\nu_{pm})}{(1 + \nu_{pm})} - \frac{2(1 - 2\nu_{LTO})K_{LTO}}{(1 + \nu_{LTO})K_{pm}}\right)}{K_{LTO} + \frac{2(1 - 2\nu_{LTO})K_{LTO}}{(1 + \nu_{LTO})K_{pm}}(\phi_{LTO}K_{LTO} + \phi_{pm}K_{pm})}$$	(13)
$$\gamma = \frac{2\lambda^* - 1}{\lambda^*}$$	(14)
$$\varepsilon_{ce} = \epsilon_{LTO}\phi_{LTO} + \left(\frac{\varepsilon_{LTO}}{\frac{1}{K_{pm}} - \frac{1}{K_{LTO}}}\right)\left(\frac{1}{K_e} - \frac{1}{K_{average}}\right)$$	(15)
$$\varepsilon_{average} = \varepsilon_{LTO}\phi_{LTO} + \phi_{pm}\varepsilon_{pm}$$	(16)
$$\frac{1}{K_{average}} = \frac{\phi_{LTO}}{K_{LTO}} + \frac{\phi_{pm}}{K_{pm}}$$	(17)

Table 3: Nomenclature for the Equations

Abbreviation	Definition
LTO	lithium titanate
ce	Composite Electrode
cc	Conductive carbon
cmc	Carboxymethyl cellulose binder
pm	Porous matrix

Table 4: List of variables and their descriptions in the model

Variable	Definition
K_m	bulk modulus of the matrix of carbon black and CMC binder particles
K_{cc}	bulk modulus of the conductive carbon (Super P)
K_{cmc}	bulk modulus of the CMC binder
G_m	shear modulus of matrix of carbon black and CMC binder particles
G_{cc}	shear modulus of the conductive carbon
G_{cmc}	shear modulus of the CMC binder particles
$\phi_{m,cc}$	Volume fraction in the conductive carbon/CMC matrix of the conductive carbon
$\phi_{m,cc}$	Volume fraction in the conductive carbon/CMC matrix of the CMC
K_{pm}	bulk modulus of a porous matrix of with solid components conductive carbon and CMC binder
ν_{pm}	Poisson's ratio of the porous matrix, assumed to be 1/3[1]
ρ_{pm}	Density of the porous matrix consisting of conductive carbon, CMC binder, and porosity
ρ_m	Density of the solid matrix consisting of conductive carbon and CMC binder
ρ_{cc}	Density of the conductive carbon (Super P)
ρ_{cmc}	Density of the CMC binder
$\phi_{pm,cc}$	Volume fraction of the conductive carbon in the porous matrix of the conductive carbon and CMC
$\phi_{pm,cmc}$	Volume fraction of the CMC binder in the porous matrix of the conductive carbon and CMC binder
ϕ_{cmc}	Volume fraction of the CMC binder in the composite electrode
ϕ_{cc}	Volume fraction of the conductive carbon in the composite electrode
ϕ_{pm}	Volume fraction of the CMC, conductive carbon, and the porosity in the composite electrode
ϕ_p	Porosity within the composite electrode
ϕ_{LTO}	Volume fraction of the iron phosphate within the composite electrode
K_{ce}	Bulk modulus of the composite electrode
ν_{LTO}	Poisson's ratio of the lithium titanate
K_{LTO}	Bulk modulus of particles in lithium titanate
λ^*	Critical volume fraction for close packing of the particle filler, 2/3
Ψ	Correction factor term
ϵ_{ce}	Linear strain of composite electrode
$\epsilon_{average}$	Average linear strain during sodiation
ϵ_{pm}	Linear strain of the porous matrix
ϵ_{LTO}	Linear strain of the lithium titanate during sodiation
$K_{average}$	Average bulk modulus of the composite electrode

Table 5: Strain changes in various voltage windows during discharge from Figure 2

Discharge Number	3.0 – 1.0 V	1.0 – 0.80 V	0.80 – 0.50V	0.50 – 0.35V
6th discharge strains	-0.015%	0.046%	0.48%	0.35%
7th Discharge strains	-0.034%	0.021%	0.32%	0.24%

Table 6: Strain changes in various voltage windows during charge from Figure 2

Charge Number	0.35 – 1.1V	1.1 – 1.55V	1.55 – 3.0 V
6th charge strains	-0.17%	-0.345%	-0.044%
7th charge strains	-0.15%	-0.250%	-0.040%

References

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6 Materials Project $Li_4Ti_5O_{12}$, https://next-gen.materialsproject.org/materials/mp-685194?formula=Li4Ti5O12, (accessed January 30, 2026).

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