Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels. This journal is © The Royal Society of Chemistry 2022

# Supplementary data

#### Determination of bulk Li<sup>+</sup> ion diffusion coefficient by Cyclic voltammetry •

From Randles Sevcik Equation

$$D = \left[\frac{slope}{26800 \times n^{3/2} \times A \times C}\right]^{2}$$
  
Diffusion coefficient,  
$$D = \left[\frac{slope}{26800 \times n^{3/2} \times A \times C}\right]^{2}$$
  
Anodic slope =  $0.00249 \frac{A}{(Vs^{-1})^{1/2}}$  [figure S4(b)]  
Cathodic slope =  $0.00264 \frac{A}{(Vs^{-1})^{1/2}}$  [figure S4(b)]  
 $n \rightarrow number of electrons trensferred in the redox event = 3$   
 $A \rightarrow electrode area in cm^{2} = 1.5 cm^{2}$   
 $C \rightarrow Concentration of electrolyte, 1M LiPF_{6} = 10^{-3} mol cm^{-3}$   
 $D_{Li^{+}}$  lithiation =  $1.5 \times 10^{-10} cm^{2} s^{-1}$   
 $D_{Li^{+}}$  delithiation =  $1.42 \times 10^{-10} cm^{2} s^{-1}$ 

# Determination of bulk Li<sup>+</sup> ion diffusion coefficient from Warburg tail of EIS Nyquist

plot

$$D_{Li^{+}} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2}$$

 $R \rightarrow gas \ constant = 8.314 \ J \ mol^{-1} K^{-1}$ 

 $T \rightarrow absolute \ temperature = 298.16 \ K$ 

 $A \rightarrow electrode area in cm^2 = 1.5 cm^2$ 

 $C \rightarrow Concentration of electrolyte, 1M LiPF_6 = 10^{-3} mol cm^{-3}$ 

 $n \rightarrow number of electrons trensferred in the redox event = 3$ 

 $F \rightarrow Faraday \ constant = 96,485 \ Cmol^{-1}$ 

 $\sigma \rightarrow Warburg \ coefficient$ = slope of the graph between the real impedance and the inverse square root of a = 76.947 \Omega s^{-1}

[figure S4(d)]

 $D_{Li^+} = 3.28 \times 10^{-14} \, cm^2 \, s^{-1}$ 

## • Solid-state diffusion coefficient of Li within the particle at different levels of

### prelithiation

$$D_{Li^{+}} = \frac{R^2 T^2}{2A^2 n^4 F^4 C_{Li^{+}}^2 \sigma^2}$$

 $C_{i,i}^{+} \rightarrow Concentration of Li^{+} in the solid phase of electrode$ 

$$C_{Li^{+}} = \frac{4 + 3x}{459.08 \ gmol^{-1}} \times 3.38 \ gcm^{-3}$$

459.08  $gmol^{-1} \rightarrow Molecular$  weight of LTO

 $3.38 \text{ gcm}^{-3} \rightarrow \text{Density of } LTO$ 

 $x \rightarrow$  stoichiometric amount of Li inserted in LTO corresponding to % DOD

Prelithiation level	Value of x	C <sub>Li</sub> +(mols cm <sup>-3</sup> )	$\begin{bmatrix} D_{Li} + (\mathbf{cm}^2 \mathbf{s}^{-1}) \\ \text{[figure S5(b)]} \end{bmatrix}$
No prelithiation ( $Li_4Ti_5O_{12}$ )	0	0.0294	$1.74 \times 10^{-17}$
30 min (Li <sub>5</sub> Ti <sub>5</sub> O <sub>12</sub> )	0.33	0.0368	$7.7 \times 10^{-18}$
60 min (Li <sub>6</sub> Ti <sub>5</sub> O <sub>12</sub> )	0.66	0.044	7.04 × 10 <sup>-18</sup>
Complete Prelithiation (Li <sub>7</sub> Ti <sub>5</sub> O <sub>12</sub> )	1	0.515	$1.7 \times 10^{-17}$

#### Formulas used for the assembly of AC/LTO LICs

#### • Preparation of the AC electrode:

• According to the Mass loading formula

 $Q = q_{positive} * m_{positive} = q_{negative} * m_{negative}$ 

Where Q=Discharge (mAh)

q=Specific capacity in second discharge cycle (mAh g<sup>-1</sup>)

m=mass of active material in the electrode

### • Energy and Power Density calculation:

- Charge Q, (mAh) = Current (mA) \* time (h)
- Capacity C,  $(mAh g^{-1}) = Q/m$ 
  - m= total mass of active material in both the electrodes
- The energy density  $(Wh kg^{-1}) = C^*V$ 
  - V= Intersecting voltage of the second charge-discharge curve.
- Power Density= Energy density/time (h)



Figure S1: The XRD pattern of commercial LTO material along with Rietveld refinement.



Figure S2: Cyclic stability of Li/LTO half-cells at a current density of 1 A  $g^{-1}$ .



Figure S3: CV profile of Li/LTO half-cell within the potential window of 1-2.75 V vs. Li<sup>+</sup>/Li at 0.1 mV s<sup>-1</sup> (first four cycles).



Figure S4: (a) CV profile of Li/LTO half-cell at different scan rates (0.1-1 mV s<sup>-1</sup>), (b) plot of anodic and cathodic peak current  $({}^{i}p)$  versus square root of scan rate $(\sqrt{v})$ ), (c) EIS Nyquist plot of Li/LTO half-cell within the frequency range of 10 kHz to 1 Hz, and (d) Real impedance versus inverse square root of angular frequency in the Warburg tail region.



Figure S5: (a) EIS Nyquist plot of Li/LTO half-cell with different levels of prelithiation (0, 30, 60 & 90 min) within the frequency range of 10 kHz to 10mHz, and (b) Real impedance versus inverse square root of angular frequency in the Warburg tail region.



Figure S6: (a, b, c & d) Potential vs. time graph of the assembled LICs at different current rates (0.05-2 A g<sup>-1</sup>), and (e, f, g, h) the CV profile of assembled LICs at different scan rates (1, 3 & 5 mV s<sup>-1</sup>).



Figure S7: Equivalent circuit model used to fit EIS Nyquist plots recorded for the assembled LIC configurations within the frequency limit of 10 kHz to 10 mHz