Supporting Information for

Covalent Organic Framework-Regulated Ionic Transportation for High-Performance Lithium-Ion Batteries

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Figure S1. Electronic arrangement of transition metal ions on 3d orbit.
Figure S2. TMI contents detected on lithium anode of Li[Li_{0.2}Mn_{0.55}Ni_{0.15}Co_{0.1}]O_2/Li coin cells after 1000 cycles. The cells were charged and discharged between 4.8 and 2 V (vs. Li/Li^+) at 0.1 C (1 C = 200 mA h g^{-1}) for the first three cycles and at 0.5 C for the remaining cycles.
Figure S3. TMI contents detected on Li anode after cycling (a) H-type Li[Li_{0.2}Mn_{0.55}Ni_{0.15}Co_{0.1}]O_{2}/Li cell voltammetrically between 2 and 4.8 V (vs. Li/Li^+) under 0.1 mV s^{-1} for (b) 80 and (c) 120 times
Figure S4. Chronoamperometric responses under a polarization of 20 mV and electrochemical impedance spectra before and after polarization for the Li/Li cells using (a,b) PS, (c,d) PS@COF and (e,f) PS@PVDF. (g) Equivalent circuit for fitting the electrochemical impedance spectra.

Table S1. Li\(^+\) transference numbers in different separators, determined from Vincent-Bruce Equation

<table>
<thead>
<tr>
<th></th>
<th>(I_{\text{initial}}) (mA)</th>
<th>(I_{\text{steady}}) (mA)</th>
<th>(R_{\text{int}}) (\text{initial}) (Ω)</th>
<th>(R_{\text{int}}) (\text{steady}) (Ω)</th>
<th>(t_{\text{Li}^+})</th>
<th>(t_{\text{PF}^6})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>0.09015</td>
<td>0.07519</td>
<td>185.03</td>
<td>168.63</td>
<td>0.38</td>
<td>0.62</td>
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<tr>
<td>PS@COF</td>
<td>0.16279</td>
<td>0.14399</td>
<td>81.54</td>
<td>84.76</td>
<td>0.76</td>
<td>0.24</td>
</tr>
<tr>
<td>PS@PVDF</td>
<td>0.04229</td>
<td>0.03627</td>
<td>445.36</td>
<td>413.9</td>
<td>0.20</td>
<td>0.80</td>
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</table>

The determination of Li\(^+\) transference number is based on Vincent-Bruce Equation:\(^1,\)\(^2\)

\[
t_{\text{Li}^+} = \frac{l_{\text{steady}} \times (V - I_{\text{initial}} \times R_{\text{int}}^{\text{initial}})}{l_{\text{initial}} \times (V - I_{\text{steady}} \times R_{\text{int}}^{\text{steady}})}
\]

where \(l_{\text{initial}}\) and \(l_{\text{steady}}\) represent initial current and steady-state current recorded during potentiostatic polarization (Fig.S4a,c,e), \(R_{\text{int}}^{\text{initial}}\) and \(R_{\text{int}}^{\text{steady}}\) represent the interfacial resistances before and after polarization, obtained from fitting the electrochemical
impedance spectra (Fig. S4b,d,f) with the equivalent circuit (Fig. S4g). In Fig. S4g, $R_b$ represents solution bulk resistance, while $R_{ct}$ and $R_f$ are the resistances of charge transfer and the film on electrode, respectively. Therefore, the interfacial resistance is the sum of $R_{ct}$ and $R_f$. The obtained Li$^+$ transference numbers are presented in Table S1.

![Impedance Spectra](image)

**Figure S5.** Electrochemical impedance spectra of SS/SS cells with (a) PS and (b) PS@COF. (c) Ionic conductivity at various temperatures and linear fitting with the Arrhenius equation.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$R_b$ (Ω)</th>
<th>$\delta$ (mS cm$^{-1}$)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$\tilde{\delta}$ (mS cm$^{-1}$)</th>
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<tr>
<td>25</td>
<td>1.68273</td>
<td>0.46707</td>
<td>3.40888</td>
<td>0.69168</td>
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<tr>
<td>30</td>
<td>1.59606</td>
<td>0.49243</td>
<td>3.11099</td>
<td>0.75791</td>
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<td>45</td>
<td>1.37016</td>
<td>0.57362</td>
<td>2.87549</td>
<td>0.81998</td>
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<tr>
<td>50</td>
<td>1.22402</td>
<td>0.64211</td>
<td>2.47129</td>
<td>0.95410</td>
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<tr>
<td>55</td>
<td>1.15583</td>
<td>0.67999</td>
<td>2.30181</td>
<td>1.02435</td>
</tr>
</tbody>
</table>

**Table S2.** Ionic conductivity based on electrochemical impedance spectroscopy.

Symmetrical stainless steel cell, SS/PS/SS and SS/PS@COF/SS, were assembled to measure the ionic conductivity ($\delta$) of the separators based on electrochemical impedance spectroscopy:

$$\delta = \frac{d}{R_b S}$$

where $R_b$ is the bulk resistance, the the value at the intersect of spectra (Fig. S5a,b) with X-axis at high frequency, $d$ and $S$ are the thickness and area of the separator, respectively. The obtained results are presented in Table S2. Apparently, the ionic conductivity of the PS can be highly
improved by coating COF. At ambient temperature (25°C), PS@COF exhibits an ionic conductivity of 0.692 mS cm⁻¹ compared to the 0.467 mS cm⁻¹ of PS. The relationship of ionic conductivity with temperature follows Arrhenius equation (Fig. S5c).

**Figure S6.** Charge/discharge performances of COF as (a) cathode and (b) anode in COF/Li cells.

COF electrodes were prepared and COF/Li cells were setup to test the charge/discharge performance of COF as anode and cathode in LIBs, using Cu and Al foils as current collectors, respectively. The cells were charged/discharged at 0.1 A g⁻¹ COF for initial three cycles and at 0.5 A g⁻¹ for the subsequent cycles, between 0 and 3 V for anode and between 2 and 4.8 V for cathode. The obtained results are presented in Fig. S6, which shows that COF electrode exhibits low specific capacity as either anode or cathode. These low capacities originated from the conductive carbon in the electrode, suggesting that COF does not exhibit lithium storage property and is electrochemically stable between 0 and 4.8 V.
Figure S7. Selected discharge profiles of Li[Li_{0.2}Mn_{0.55}Ni_{0.15}Co_{0.1}]O_2/Li cells with (a) PS and (b) PS@COF at 0.5 C.
Figure S8. SEM images of fresh Li electrode (a) and the cycled Li electrodes in Li[Li$_{0.2}$Mn$_{0.55}$Ni$_{0.15}$Co$_{0.1}$]O$_2$/Li cells with (b) PS and (c) PS@COF after 500 cycles.
Figure S9. Cycling performance of Li[Li$_{0.2}$Mn$_{0.55}$Ni$_{0.15}$Co$_{0.1}$]O$_2$/Li cells using PS and PS@COF with 5 μL electrolyte at 0.5 C.
Figure S10. Cyclic performance of NCM811/Li cells with PS and PS@COF at (a) 25°C and (b) 55°C.
Figure S11. Cycling performance of graphite/Li cells with PS and PS@COF.
Figure S12. XRD patterns of COF before (black) and after (red) cycling.

TPB-DMTP-COF exhibits the peaks at 2.76°, 4.76°, 5.58°, 7.40°, 9.68°, and 25.2°, corresponding to the (100), (110), (200), (210), (220), and (001) facets.
Figure S13. XPS profiles of (a) C 1s, (b) O 1s, (c) P 2p and (d) F 1s on graphite anode from Li[Li_{0.2}Mn_{0.55}Ni_{0.15}Co_{0.1}]O_{2}/graphite full cell before cycling (top) and after cycling with PS (middle) and PS@COF (down) for 500 times.

The C 1s spectra of the fresh graphite electrode contain three main peaks, corresponding to C-C (284.7 eV), and C-F (290.9 eV) in PVDF binder, and the peak of C-O at 286.0 eV. The peak of Li₂CO₃ at 290.4 eV can be observed on graphite with PS, while it almost vanishes for graphite with PS@COF, revealing that the decomposition of the electrolyte is suppressed by COF. C=O (532.3 eV) and C-O (534.1 eV) are detected on the fresh graphite electrode in O 1s spectra. These peaks are more obvious on the cycled graphite anode with PS than PS@COF, suggesting that there are more electrolyte decomposition products on graphite with PS. In the F 1s spectra, the peak at 687.3 eV belongs to LiPₓFᵧ, and another peak at 685.4 eV is attributed to LiF. In the P 2p spectra the peaks of LiPO_{y}F_{z} (134.2 eV) and LiPₓFᵧ (137.2 eV) can be identified. All these species are derived from electrolyte decomposition and presents stronger peaks on graphite with PS than with PS@COF, confirming the suppression of electrolyte decomposition by PS@COF.
Table S3. The element contents detected on graphite anodes from the Li[Li$_{0.2}$Mn$_{0.55}$Ni$_{0.15}$Co$_{0.1}$]O$_2$/graphite full cells with PS and PS@COF after 100 cycles, determined by mappings.

It can be seen from Table S3 that the content of Ni, Co and Mn on the graphite with PS is sharply increased after cycling, showing that TMIs is free to transport in PS. This case never happens on the graphite with PS@COF, indicating the ability of PS@COF to capture transition metal ions.
References


