**Supplementary Tables**

Table S1: Compositions of synthesized compounds, as indicated by atomic ratios measured by ICP.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Target ratio Li : Mn : V : F</th>
<th>Measured ratio Li : Mn : V : F</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-LMVO</td>
<td>1.143 : 0.286 : 0.572 : 0</td>
<td>1.155 : 0.268 : 0.571 : 0</td>
</tr>
<tr>
<td>ST-LMVF20</td>
<td>1.171 : 0.343 : 0.486 : 0.2</td>
<td>1.180 : 0.329 : 0.461 : 0.213</td>
</tr>
<tr>
<td>MR-LMVF20</td>
<td>1.133 : 0.400 : 0.467 : 0.2</td>
<td>1.141 : 0.405 : 0.474 : 0.204</td>
</tr>
<tr>
<td>LR-LMVF20</td>
<td>1.230 : 0.255 : 0.515 : 0.2</td>
<td>1.236 : 0.252 : 0.518 : 0.204</td>
</tr>
<tr>
<td>LR-LMVO</td>
<td>1.200 : 0.200 : 0.600 : 0</td>
<td>1.211 : 0.198 : 0.590 : 0</td>
</tr>
</tbody>
</table>
Supplementary Figures

Figure S1: Computed phase diagram of the MnO-Li$_3$NbO$_4$-LiF and MnO-Li$_2$TiO$_3$-LiF systems, marking the previously reported compositions successfully synthesized by high-energy ball-milling. As the reported compositions are stabilized at approximately 1750 °C, we choose stability at 1750 °C as a heuristic for synthetic accessibility by high-energy ball-milling.
Figure S2: XRD refinement and scanning electron microscopy (SEM) imaging of the secondary particles of a. ST-LMVO, b. ST-LMVF20, c. MR-LMVF20, d. LR-LMVF20, e. LR-LMVO.
Figure S3: **a.** TEM and **b.** HRTEM image and **c.** electron diffraction pattern of ST-LMVF20. The TEM image shows that the secondary particle size of the ST-LMVF20 is around 100 nm. The HRTEM image is taken within the dashed-line square area in **a.**, and we can see different oriented fringes, which indicates the particle is polycrystalline. The electron diffraction pattern shows the characteristic diffraction rings of a disordered rock-salt structure, which further proves that the as-synthesized material is a polycrystalline disordered rock-salt.
Figure S4: Galvanostatic voltage profiles for charge–discharge cycles, and associated capacity retention in a., b. ST-LMVF20 (4.6V, 4.2V cutoff), c. ST-LMVO (4.6V), d. MR-LMVF20 (4.6V), e. LR-LMVF20 (4.6V) and f. LR-LMVO (4.6V).
Figure S5: High temperature galvanocycle cycling profile of ST-LMVF20.
Figure S6: Voltage profile of first-charge samples used for XAS characterization.
The DEMS results shown in Figure S7 reveal a noticeable amount of CO$_2$ gas evolution, which can be mainly attributed to the decomposition of surface carbonate as reported previously.$^{1,2}$ However, this contribution to the overall capacity is small. Renfrew et al.$^2$ point out that surface Li$_2$CO$_3$ oxidation does contribute to the first cycle capacity, but DEMS results by W. H. Kan et al.$^3$ show that CO$_2$ evolution is greatly reduced in the second charge, indicating that Li$_2$CO$_3$ oxidation is for the most part irreversible. In our materials, while there is clearly some Li$_2$CO$_3$ oxidation, its contribution to the overall capacity must be small as we measure highly reversible performance over repeated charge/discharge cycles. The voltage profile of ST-LMVF20 shown in Fig. 3a is mostly unchanged over the first five cycles, with almost no capacity fade and a Coulombic efficiency in excess of 94% even for the first cycle. These findings indicate that any surface Li$_2$CO$_3$ oxidation is small compared to bulk transition metal oxidation as otherwise we would observe much more obvious capacity fade and smaller Coulombic efficiency.
References

