#### ARTICLE

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Export Citation

# *In situ* cathode-electrolyte interphase enables high cycling stability of Co-free Li-rich layered cathodes

Cite as: APL Energy 1, 026101 (2023); doi: 10.1063/5.0150919 Submitted: 16 March 2023 • Accepted: 7 June 2023 • Published Online: 5 July 2023

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#### ABSTRACT

Despite the extensive research in Li-rich layered oxides (LLOs), which are promising candidates for high-energy density cathodes, their cycle life still cannot meet the real-world application requirements. The poor cycle performance arises from the electrolyte decomposition at high voltage, resulting in damage and subsequent surface-initiated conversion of the cathode from layered to spinel phase. This problem is even more challenging for Co-free LLO cathodes. Here, we report a one-pot synthesis of *in situ* carbonate-coated nanostructured Co-free LLO (Li<sub>2</sub>CO<sub>3</sub>@LLO) through a polyol-assisted method. This inorganic coating suppresses oxygen release, provides good Li-ion transport, and protects the cathode from adverse reactions with the electrolyte. The obtained material exhibits excellent long-term stability, with 76% capacity retention after 1000 cycles at a 0.2 C rate without any Co addition, demonstrating a path forward for using LLOs as a next-generation Li-ion battery cathode.

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#### INTRODUCTION

Co-free Li-rich layered oxides  $[yLi_2MnO_3 \cdot (1 - y)LiNi_{1-x}Mn_xO_2$  (LLO)] have been considered promising high-energy density cathode materials as high as 400 Wh kg<sup>-1</sup> due to reversible oxygen redox in addition to the usual transition metal redox reactions.<sup>1,2</sup> However, they suffer from fast voltage decay, low rate capability, and poor cycling stability, less than 500 cycles.<sup>3-6</sup> The poor cycle performance is widely accepted to originate from the progressive surface-initiated transition from the layered to the spinel phase, assisted by the dissolution and migration of transition metal ions.<sup>4-8</sup>

To achieve the high energy density, the  $Li_2MnO_3$  component must be activated under a high charge voltage of 4.8 V to extract secondary Li–ions from the transition metal layers, accompanied by oxygen anionic redox,<sup>9</sup> while the low practical voltage cut-off of carbonate electrolytes (~4.5 V) leads to their oxidation and decomposition. Meanwhile, the oxidation of surface oxygen results in irreversible  $O_2$  gas release, accelerating the side reactions and oxidation of electrolytes at high voltage and causing the formation of a thick, fragile, and inhomogeneous organic-rich cathode-electrolyte interphase (CEI) layer on the cathode surface. Furthermore, decomposition products, especially HF, trigger the dissolution of metal ions on the surface and jeopardize cycle stability, accompanied by surface-initiated conversion from the layered to the spinel phase.<sup>6,10</sup>

Hence, most research efforts including structural changes,  $^{4,11-14}$  surface engineering,  $^{15-19}$  element doping,  $^{15,20-22}$  and the use of electrolyte additives  $^{6,23,24}$  have been dedicated to mitigating the mentioned problems. However, cycling stability for modified LLO remains bound by ~500 cycles<sup>6</sup> and still does not meet the real-world application requirements.

Considering the surface origin of LLO structural degradation, protection from undesired side reactions at the surface can be a promising strategy,<sup>25</sup> specifically if a robust surface protection in the

form of artificial CEI could be found. Previous works reported that CEIs composed of inorganic components such as  $CaCO_3$ ,<sup>26</sup> AlF<sub>3</sub>,<sup>27</sup> and concentrated electrolyte (3M LiPF<sub>6</sub>)<sup>6</sup> improve the cycle stability of cathodes, unlike CEIs containing organic components, which possess an insulating nature, low electron transfer, and enhance the dissolution of transition metals.<sup>6,28</sup> Li<sub>2</sub>CO<sub>3</sub> artificial CEI is one such example of a coating that would also be chemically stable, mitigate mechanical degradation, and facilitate Li–ion transport,<sup>28</sup> but it has not yet been explored for LLO stabilization purposes.

Here, we demonstrate that an *in situ*, evenly carbonate-coated nanostructured LLO (Li<sub>2</sub>CO<sub>3</sub>@LLO) exhibits excellent stability as a Li–ion battery cathode. We chose a Co-free Na-doped high-Ni LLO material because of its high capacity, low cost, and low toxicity.<sup>22,29</sup> We characterized this stable inorganic-rich CEI using field emission scanning electron microscopy with energy dispersive spectroscopy (FESEM-EDS), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and electrochemical impedance spectroscopy (EIS) measurements. We further confirm that this carbonate coating protects the surface from the layered-to-spinel transition using galvanostatic charge-discharge and cyclic voltammetry (CV) tests. The obtained material demonstrates excellent durability after ultra-long cycling (~1000 cycles) for Li-rich cathodes.

# **RESULTS AND DISCUSSION**

We aimed to develop a method that would have an *in situ* CEI pre-formed and explored multiple syntheses. We employed the polyol method, where ethylene glycol acts as a solvent, reducing and chelating agent, and carbon source for the coating. This technique provided monodisperse nanoparticle morphology and *in situ* carbonate coating without using any post-treatment.<sup>30,31</sup>

The schematic of the synthesis procedure and mechanism of carbonate coating on the LLO are displayed in Fig. 1, which consist of chelation and hydrolysis of transition metal ions, Mn<sub>2</sub>NiO<sub>4</sub> formation, and Li2CO3@LLO production. During the dissolution of the MnCl<sub>2</sub> and NiCl<sub>2</sub> salts in the first step of the polyol process, ethylene glycol coordinated with transition metal chlorides. Then, in the second step, the NaOH solution in ethylene glycol was used as a hydrolysis agent of metal ions, in which deprotonation of ethylene glycol can occur. After adding the hydroxide solution, the substitution of chloride ions with hydroxyl groups leads to the formation of Mn and Ni hydroxides. As a result, the product of the polyol process is the chelated Mn<sub>2</sub>Ni(OH)<sub>4</sub>, as revealed by Mn/Ni ratio measurements using ICP-OES. Afterward, the transition metal oxide can be formed by the calcination of the hydroxide precursor [Eq. (1)]. During this process, some of the ethylene glycol and its deprotonated molecules can be transformed into carbon by releasing CO2 and H<sub>2</sub>O.

The mechanism of  $Mn_2NiO_4$  formation is shown in detail in Fig. S1. To investigate the reaction mechanism of the Li<sub>2</sub>CO<sub>3</sub>@LLO formation, X-ray diffraction (XRD) was applied to the carbon coated  $Mn_2NiO_4$  (denoted as C@Mn\_2NiO\_4) precursor and final Li<sub>2</sub>CO<sub>3</sub>@LLO product. The XRD patterns show that the transition metal oxide can be formed after the calcination of the polyol product [Fig. 2(a)]. All the diffraction peaks of C@Mn\_2NiO\_4 can be well indexed to  $Mn_2NiO_4$  (JCPDS No. 00-001-1110). In the final step, after  $Mn_2NiO_4$  mixing with LiOH, followed by calcination, the LLO, Li<sub>2</sub>CO<sub>3</sub>, residual carbon, and C-H-O products were obtained according to Eqs. (2) and (3). The characteristic XRD peaks of LLO are indexed to combined patterns of Li<sub>2</sub>MnO<sub>3</sub> (JCPDS No. 00-027-1252) and standard values of the LiMO<sub>2</sub> phase (JCPDS No. 01-087-1564), as shown in Fig. 2(a). The peaks around 21°-22° indicate the existence of Li<sub>2</sub>MnO<sub>3</sub> as a layered Li-rich phase,

$$Mn_2Ni(OH)_4 + O_2 \rightarrow Mn_2NiO_4 + 2H_2O,$$
(1)



FIG. 1. Schematic and mechanism of the polyol-assisted method to synthesize  $Li_2CO_3$ @LLO. The synthesis procedure includes (1) chelation of transition metal ions  $[Mn_2Ni(OH)_4]$  and (2) their hydrolysis using NaOH; and (3)  $Mn_2NiO_4$  formation after calcination of the hydroxide sample. During this process, ethylene glycol and its deprotonated molecules are converted to carbon; and (4)  $Li_2CO_3$ @LLO production through mixing with LiOH, followed by calcination at 900 °C.



FIG. 2. Structural and chemical characterization of the C@Mn<sub>2</sub>NiO<sub>4</sub> precursor and final Li<sub>2</sub>CO<sub>3</sub>@LLO product. (a) XRD patterns for the precursor and final product. The standard Bragg positions of Li<sub>2</sub>MnO<sub>3</sub> and LiTMO<sub>2</sub> (TM = transition metal) phases are also indicated. Based on these results, the precursor after the calcination of the synthesized polyol sample is Mn<sub>2</sub>NiO<sub>4</sub>, and the final product is Li-rich layered oxide, according to the weak peaks located at ~21°. (b) Ratio-stacked bar chart of the surface and bulk of Li<sub>2</sub>CO<sub>3</sub>@LLO measured by XPS and ICP-OES results, respectively, indicating the excess Li on the LLO surface is related to the Li<sub>2</sub>CO<sub>3</sub> shell.

$$y\mathrm{Mn_2NiO_4} + x\mathrm{LiOH} \rightarrow \mathrm{Li}_x(\mathrm{Mn_2Ni})_y\mathrm{O_2} + \frac{x}{2}\mathrm{H_2O} + \left(2y + \frac{x}{4} - 1\right)\mathrm{O_2},$$
(2)

$$2\text{LiOH} + \text{C} + \text{O}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O}.$$
 (3)

The bulk and surface chemical compositions of the final product using ICP-OES/EDS and XPS, respectively, demonstrate that excess Li content exists on the surface of LLO, unlike conventional synthesis, which loses Li on the surface of LLO due to its evaporation [Fig. 2(b)]. These results indicate that a Li-excess phase is present on the LLO surface, whose nature was further studied by FESEM and FTIR measurements. Based on elemental analysis (ICP-OES and EDS), Li<sub>2</sub>CO<sub>3</sub>@LLO was prepared by the following reaction [Eq. (4)]. Therefore, the results revealed that the weight ratio of Li<sub>2</sub>CO<sub>3</sub>:LLO is ~0.04,

$$0.24 \text{ Mn}_{2.6}\text{Ni}(\text{Na}_{0.005})\text{O}_4 + 1.23 \text{ LiOH} + x\text{O}_2 + y\text{C} + z(hydrocarbons: \text{C}_2\text{H}_4\text{O}_2, ...) \rightarrow \text{Li}_{1.13}(\text{Na}_{0.005})\text{Mn}_{0.625}\text{Ni}_{0.24}\text{O}_2 + x_1\text{H}_2\text{O} + 0.05\text{Li}_2\text{CO}_3 + 0.3\text{C} + y_1\text{CO}_2 + z_1(hydrocarbons: \text{C}_2\text{H}_4\text{O}_2, ...).$$
(4)

The FESEM images show that the obtained  $C@Mn_2NiO_4$  precursor consists of nanoparticles of ~10 nm [Fig. 3(a)], linked together and homogenously distributed in some non-crystalline medium in most areas. The EDS elemental mapping result for the precursor is shown in Fig. S2, indicating a uniform distribution of each element, primarily carbon, in the sample. The FESEM, TEM, and EDS mapping results of the final  $Li_2CO_3@LLO$  product [Figs. 3(b), 3(c), and 3(e), respectively] exhibit that an amorphous carbonaceous shell (~10 nm) was produced on the surface of LLO grains, and LLO nanoparticles (~100 nm) were successfully enclosed by the shell, as marked by the arrows. Figure 3(d) is a schematic of produced carbonate shell on the LLO. Moreover, the EDS elemental mappings demonstrate the uniform distributions of Na, Ni, and Mn (as shown in Fig. S3).

The FTIR spectrum consists of a peak in the region around 1640 cm<sup>-1</sup> of C@Mn<sub>2</sub>NiO<sub>4</sub> and Li<sub>2</sub>CO<sub>3</sub>@LLO, which is ascribed to the characteristic peak of  $carbon^{32}$  [Fig. 3(f)]. Carbon on the oxide materials can be obtained using ethylene glycol and/or other carbon sources under a reducing/inert atmosphere<sup>33,34</sup> or low oxygen partial pressure.<sup>35</sup> The oxidation of carbon at temperatures above 700 °C depends on oxygen partial pressure and, therefore, under its low values, the carbon coating may have been produced.<sup>36</sup> Moreover, the sharp characteristic peaks located around 869, 1643, and 1500 cm<sup>-1</sup> are attributed to lithium carbonate.<sup>37</sup> These results imply that carbon is present in the Mn<sub>2</sub>NiO<sub>4</sub> precursor, and then a Li<sub>2</sub>CO<sub>3</sub> shell can be formed on the surface of LLO due to the reaction of carbon with LiOH during the heat-treatment process, as previously discussed in the synthesis mechanism. Therefore, because the synthesis temperature (900 °C) is above the melting point of Li<sub>2</sub>CO<sub>3</sub> (723 °C), this component acts as a flux above ~700 °C and is coated on the LLO surface. The weight ratio of Li<sub>2</sub>CO<sub>3</sub>:LLO, ~4%, is greater than the detection limit of XRD, which is ~2% for mixed materials. However, the characteristic XRD peaks of carbon and Li<sub>2</sub>CO<sub>3</sub> at 25° and 21° are not observed in C@Mn<sub>2</sub>NiO<sub>4</sub> and Li<sub>2</sub>CO<sub>3</sub>@LLO, indicating their amorphous character (Fig. S4). In addition, in the oxygen 1s XPS spectra (Fig. S5 and supplementary



FIG. 3. Characterization of the amorphous shell on the LLO. (a) and (b) FESEM images of the C@Mn<sub>2</sub>NiO<sub>4</sub> and Li<sub>2</sub>CO<sub>3</sub>@LLO, respectively; (c) TEM image of the Li<sub>2</sub>CO<sub>3</sub>@LLO; (d) schematic of the carbonate amorphous shell on the LLO; (e) EDS elemental mapping of the Li<sub>2</sub>CO<sub>3</sub>@LLO; (f) FTIR results of the as-prepared C@Mn<sub>2</sub>NiO<sub>4</sub> precursor and the final Li<sub>2</sub>CO<sub>3</sub>@LLO product, which exhibits the sharp characteristic peaks of Li<sub>2</sub>CO<sub>3</sub>.

material Note 1), the sharp peak at 532.5 eV corresponds to the  $-CO_3$  polyanions, whose intensity is higher than the lattice oxygen and oxygen vacancy. This result is consistent with FESEM and FTIR findings, which verify that the carbonate shell was successfully formed on the surface of LLO.

Galvanostatic charge-discharge measurements were carried out at a 0.1 C rate (1 C = 200 mA  $g^{-1}$ ) to investigate the electrochemical performance of the Li<sub>2</sub>CO<sub>3</sub>@LLO electrode [Figs. 4(a) and 4(b)]. The lower-voltage Mn<sup>4+</sup>/Mn<sup>3+</sup> redox at ~2.7 V has been assigned to structural degradation from the layered to the spinel phase transition.<sup>5</sup> This reduction occurs upon displacement of Li<sup>+</sup> from tetrahedral to 16c octahedral sites, which is associated with the transformation of spinel  $Li_{2-x-y}[Ni_xMn_y]O_4$  to tetragonal phase and attributed to the Jahn-Teller distortion of Mn<sup>3+</sup> ions.<sup>38</sup> Selected charge-discharge curves of the Li2CO3@LLO cathode at 0.2 and 0.1 C are displayed in Figs. 4(b) and S7, respectively, which indicate a very small  $Mn^{4+}/Mn^{3+}$  redox even after 800 cycles. The Li<sub>2</sub>CO<sub>3</sub>@LLO electrode shows excellent cycling stability with 99% capacity remaining over 200 cycles at a 0.1 C rate, 88% capacity retention after 600 cycles at a 0.2 C rate, and 76% capacity remaining after ~1000 cycles at a 0.2 C rate by supporting the reversible transition metal redox and mitigating the layered-to-spinel phase transition. Moreover, the Li<sub>2</sub>CO<sub>3</sub>@LLO electrode delivered a first energy density of 560 Wh kg<sup>-1</sup> at 0.1 C with an energy density retention of 63% (311 Wh kg<sup>-1</sup>) after 1000 cycles at 0.2 C [Fig. 4(a)]. Another important feature of Li2CO3@LLO is its good rate capability with a maximum discharge capacity of about 138.1 mAh g<sup>-1</sup> at a 0.2 C rate, 121.8 mAh g<sup>-1</sup> at a 0.5 C rate, and 104.7 mAh g<sup>-1</sup> at a 1 C rate, respectively.

The kinetic behavior is further investigated utilizing the EIS analyses from the samples after equilibrium at a charged state of

4.8 V at 0.1 C from the 1st and 10th to 60th cycles [Fig. 4(c)]. An entire Li-ion battery cell can be modeled using an equivalent circuit shown in Fig. S8, in which the R<sub>b</sub>, R<sub>CEI</sub>, and R<sub>ct</sub> stand for the internal resistance, CEI resistance, and charge transfer resistance, respectively.<sup>39</sup> CEI is generated by the decomposition of the electrolyte, whose resistance is extremely sensitive to the reactivity of the electrolyte during the first lithiation cycle, which released oxygen and Mn dissolution could affect its reactivity. The fitting results for the Li2CO3@LLO electrode show that the RCEI decreases with the increasing cycle from 1st to 10th due to the transport of trapped Li ions in the CEI after the first charge, and minor changes are observed to cycle 60th. The R<sub>CEI</sub> results indicate that the carbonate shell effectively captures the active oxygen released and reduces electrolyte decomposition, which coincides with the excellent structural stability of the sample. Furthermore, the Rct of the Li2CO3@LLO electrode does not change significantly during cycling. Eventually, the surface resistance could be effectively decreased with the surface modification and designed structure, possibly deriving from the suppression of fast CEI growth, which will be favorable for the electrochemical performance of the LLO electrode.

Moreover, the corresponding CV experiment of the cathode [Fig. 4(d)] confirms the formation of a layered LLO phase, indicating the anodic peaks at ~4.15/4.3 V and ~4.6 to 4.8 V are ascribed to the Ni<sup>2+</sup>/Ni<sup>4+</sup> and oxygen redox, respectively. As such, the reduction redox peaks at ~4.2, 3.7, and 3.2 V are attributed to the  $O_{2p}$ , Ni<sup>2+</sup>/Ni<sup>4+</sup>, and  $O^{2-/n^-}$  redox, respectively. Although there is an irreversible oxygen redox above 4.6 V, especially in the first charge during the Li<sub>2</sub>MnO<sub>3</sub> activation process, the Li<sub>2</sub>CO<sub>3</sub> coating would serve as an artificial CEI layer,<sup>40</sup> reduce the activity of released oxygen,<sup>41</sup> and restrict the undesirable surface side reaction occurring at the electrode–electrolyte interface. For emphasizing the occurring



FIG. 4. Structural stability of the  $Li_2CO_3@LLO$  after long-term cycling. (a) Cyclic performance at 0.2 C rate and rate capability of the  $Li_2CO_3@LLO$  electrode when cycling between 2.0 and 4.8 V at various rates from 0.1 to 1 C rate; (b) Selected charge-discharge at 0.2 C rate; (c) CEI stability of the cathode based on EIS measurement; (d) CV plots for  $Li_2CO_3@LLO$  cathode at 1 mV/s after long-term cycling; and (e) schematic diagram of crystal structures for synthesized  $Li_2CO_3@LLO$  during synthesis, compared with conventional layered Li oxide cathodes, and impact of the produced shell to inhibit the layered-to-spinel transition.

redox processes, the CV profile of the Li<sub>2</sub>CO<sub>3</sub>@LLO electrode during extensive cycling exhibits that the oxygen and Ni redox are almost constant during cycling. In addition, the  $Mn^{4+}/Mn^{3+}$  redox related to the spinel phase is not observed after 50 cycles at 1 mV/s. It is worth mentioning that both carbon and carbonate shells before and after final calcination, respectively, also act as a spacer

that prevents the fusion of nanoparticles.<sup>30,31</sup> Nanostructured LLO morphology helped to achieve the intercalation-pseudocapacitance behavior of Li<sup>+</sup> due to the short diffusion lengths,<sup>42</sup> which is beneficial for cycling stability and avoiding the crystallographic phase change<sup>42,43</sup> (see the supplementary material, Fig. S9 and Note 2). Furthermore, the different synthesis parameters using this same

polyol-assisted method have been studied in our previous report.<sup>14</sup> The overall results indicated that only the coated samples significantly improved stability, even though other samples with enhanced oxygen vacancies led to increased capacity but not cycling stability.

On the basis of all the above-mentioned results, a schematic diagram [Fig. 4(e)] is used to further illustrate the crystal structures of the  $Mn_2NiO_4$  precursor and synthesized Li<sub>2</sub>CO<sub>3</sub>@LLO compared with layered cathodes, which implies that the Li-rich structure as a high-voltage and high-capacity electrode has a high-energy density. This study presents Li<sub>2</sub>CO<sub>3</sub> shells that effectively inhibit the layered to low-voltage spinel transition and improve structural stability.

# CONCLUSION

In summary, a facile and effective strategy to improve the battery cycle life was proposed by employing carbonate coated nanostructured LLO via the polyol-assisted method. As confirmed by structural analysis such as FESEM, EDS, FTIR, XRD, ICP-OES, and XPS, the polyol decomposition products remain in the cathode, starting from the Mn<sub>2</sub>NiO<sub>4</sub> precursor, then react with LiOH and form a protective carbonate shell during the heat-treatment process. Galvanostatic cycling/CV/EIS results demonstrate the structural integrity of target material over long-term cycling, which was ascribed to modified CEI. The inorganic carbonate shell serves as an even and homogeneous artificial CEI, acts as a barrier against severe interfacial reactions, captures the active oxygen released, and inhibits electrolyte decomposition. This study reveals that in situ carbonate-coated Co-free LLO can suppress the layered-to-spinel phase transition and make a promising Li-ion battery cathode for application in long-cycle life and high-energy-density energy storage systems.

#### METHODS

## Synthesis of Li<sub>2</sub>CO<sub>3</sub>@LLO

Synthesis of manganese nickel oxide precursor (C@Mn<sub>2</sub>NiO<sub>4</sub>): 0.25M manganese (II) chloride tetrahydrate, 0.083M nickel (II) chloride hexahydrate, and 0.5M sodium hydroxide were added to 20 ml of ethylene glycol with molar ratios of 0.6:0.2:1.2. The solution was stirred at a constant temperature of 180 °C for 20 h in a 50-ml flask connected to a reflux condenser. The obtained mixture was washed with deionized water and ethanol several times, followed by drying in an oven at 80 °C overnight. As-prepared precipitate was then annealed in air at 500 °C at a rate of  $3.5 ^{\circ}$ C min<sup>-1</sup> for 6 h.

Synthesis of Li<sub>2</sub>CO<sub>3</sub>@LLO material: the C@Mn<sub>2</sub>NiO<sub>4</sub> precursor was mixed with LiOH  $\cdot$  H<sub>2</sub>O (0.008 25 mol) and then annealed at 900 °C at a rate of 3.5 °C min<sup>-1</sup> for 12 h in a low partial pressure oxygen environment.

### Material characterization

X-ray photoelectron spectroscopy (XPS) measurement was collected using a Thermo Scientific K-Alpha to identify the chemical composition of the cathode surface. X-ray diffraction (XRD) was performed on a Rigaku-MiniFlex-6G diffractometer to investigate the crystallography phase of the cathode material. The composition of the product was confirmed quantitatively by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Axial ICP-OES, Varian. 730-ES). A field-emission scanning electron microscopy (FESEM) image in conjunction with an energy dispersive X-ray spectrometer (EDS) was acquired on a MIRA3 TESCAN. A transmission electron microscopy (TEM) image was performed on a Philips EM208S-100 kV. A Fourier-transform infrared spectroscopy (FTIR) analysis was carried out on a Unicam Matson 1000 using a pellet made of active materials and KBr powder.

#### **Electrochemical measurements**

The cathode electrode was fabricated by pasting the slurry with a mixing 80 wt. % active material, 10 wt. % conductive carbon black, and 10 wt. % poly (vinylidene fluoride) in N-methyl-2 pyrrolidone on an aluminum current collector. Then, the disk of 10-mm diameter was punched from the prepared electrode and dried at 110 °C for 10 h in vacuum. The electrochemical measurements were carried out with CR2032 coin-type cells using lithium foil as the anode, Celgard 2400 membrane as a separator, and an electrolyte solution of 1M LiPF<sub>6</sub> in a 1:1 (volume ratio) mixture of ethylene carbonate/dimethyl carbonate mixture solution (BASF). All coin-type cells were galvanostatically charged and discharged on a LAND (battery tester, China) at a current density of C/10 (1 C = 200 mA  $g^{-1}$ ) at 25 °C in the voltage ranges of 2-4.8 V. The rate performance tests were discharged at 0.1, 0.2, 0.5, and 1 C and then returned to a 0.2 C-rate. Cyclic voltammetry (CV) measurements and Electrochemical impedance spectroscopy (EIS) of the cell were performed by a VMP3 multi-channel potentiostat (Bio-Logic, France) over a frequency range from 1 MHz to 10 MHz at a pristine as well as charged state of 4.8 at different cycles.

#### SUPPLEMENTARY MATERIAL

Detailed information regarding XPS and CV analysis at different scan rates of the  $Li_2CO_3@LLO$ , electrochemical measurements, mechanism of the  $Mn_2NiO_4$  formation via polyol synthesis, EDS elemental mapping, comparison of XRD patterns of the C@Mi\_2NiO\_4 and Li\_2CO\_3@LLO with standard crystallographic databases of the Li\_2CO\_3 and carbon phases, charges-discharge voltage profiles of the Li\_2CO\_3@LLO electrode at 0.1 C, and equivalent circuit model of the Li-ion battery are shown in the supplementary material.

#### ACKNOWLEDGMENTS

S.K.S. acknowledges the support of the Iran National Science Foundation (INSF). O.V. acknowledges the financial support from the Natural Sciences and Engineering Research Council Discovery (Grant No. 2019-04897), the Canada Foundation for Innovation and Ontario Research Fund (Project No. 38101), and the University of Toronto XSeed program. Computations were performed on the Niagara supercomputer at the SciNet HPC Consortium. SciNet is funded by the Canada Foundation for Innovation, the Government of Ontario, the Ontario Research Fund – Research Excellence, and the University of Toronto.

# AUTHOR DECLARATIONS

#### **Conflict of Interest**

The authors have no conflicts to disclose.

# **Author Contributions**

**Parisa Vahdatkhah**: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Project administration (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Sayed Khatiboleslam Sadrnezhaad**: Funding acquisition (equal); Resources (equal); Supervision (equal); Writing – review & editing (equal). **Oleksandr Voznyy**: Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Resources (equal); Software (equal); Supervision (equal); Validation (equal); Writing – review & editing (equal).

#### DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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