Supporting Information

A nano-structured RuO$_2$/NiO cathode enables the operation of non-aqueous lithium-air batteries in ambient air

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Figure S1 TG curves of sample (a) Ni foam; (b) NiC$_2$O$_4$·2H$_2$O/Ni foam. To clearly see the weight change during the heat treatment, both tests were conducted in air at a heating rate of 2 °C min$^{-1}$ to 400 °C, and then kept in 400 °C for 45 min. (c) Ru(OH)$_3$·xH$_2$O/NiO foam. The test was conducted in air at a heating rate of 2 °C min$^{-1}$ to 300 °C, and then kept in 300 °C for 4 h. The inset shows the weight change during four hours. After three hours the weight almost keeps constant, suggesting that the precursor is fully converted to RuO$_2$. The initial weight of Ni is 37.201 mg cm$^{-2}$, and after calcination in 400 °C for 45 min, the weight change due to oxidization is 0.059% (2Ni + O$_2$ → 2NiO), indicating that the weight of formed NiO is 0.102 mg cm$^{-2}$ (37.201 mg cm$^{-2}$ × 0.059% × 74.7 / 16). After immersion in the oxalic acid solution, the initial weight of NiC$_2$O$_4$·2H$_2$O/Ni foam is 37.879 mg cm$^{-2}$. As shown in Fig. S1b, two weight loss processes occur at around 180 and 320 °C, representing the removal of crystal water and further decomposition of the nickel oxalate corresponding to the transformation from NiC$_2$O$_4$ to NiO with the release of CO$_2$, respectively [1]. To obtain the loading of NiO nanosheets, suppose the weight of NiC$_2$O$_4$·2H$_2$O and Ni is $x$ and $y$, respectively, and $x + y = 37.879$ mg cm$^{-2}$. After the calcination process, the weight can be calculated from Fig. R6b as $\frac{74.7}{182.7} \cdot x + 100.059\% \cdot y = 98.495\% \cdot 37.879$ mg cm$^{-2}$, resulting in $x = 1.001$ mg cm$^{-2}$, $y = 36.878$ mg cm$^{-2}$. Thus, the loading of NiO nanosheets (formed from NiC$_2$O$_4$·2H$_2$O) is 0.409 mg cm$^{-2}$, and the weight of NiO/Ni is 37.309 mg cm$^{-2}$. Fig. S1c shows the weight change of Ru(OH)$_3$·xH$_2$O/NiO in the fabrication process, and the initial weight is 37.644 mg cm$^{-2}$. After the heat treatment, the final weight of RuO$_2$/NiO is 37.644 mg cm$^{-2}$ × 99.242% = 37.358 mg cm$^{-2}$. Considering the weight of NiO/Ni (37.309 mg cm$^{-2}$), the loading of RuO$_2$ is got to be 0.049 mg cm$^{-2}$. 
Figure S2 Characterization of the RuO$_2$/Ni electrode: (a) SEM image. The inset shows the high-resolution of RuO$_2$ nanoparticles on the Ni surface; (b) Raman spectrum. Three peaks corresponding to the E$_g$, A$_{1g}$, and B$_{2g}$ Raman active modes of RuO$_2$ have been detected. In addition, the peak of one-phonon (1P) scattering of NiO can also be detected, suggesting some oxidization of Ni during the fabrication process.
Figure S3 TEM image of the NiO nanosheet: (a) The nanosheet is composed of nanoparticles, the inset shows the histograms of particle size distribution, with the average diameter of 5.14 nm; (b) the regular interplanar spacing of 2.42 and 2.08 Å is ascribed to the (111) and (200) plane of NiO (JCPDS # 40-1290), respectively. The inset shows the diffraction rings of a selected area.
Figure S4 Nitrogen adsorption-desorption isotherm of (a) Ni foam, (b) Ni foam oxidized at the similar condition for the preparation of NiO/Ni; (c) NiO nanosheet-anchored nickel foam (NiO/Ni); and (d) RuO$_2$ nanoparticle-decorated NiO nanosheets (RuO$_2$/NiO). Inset shows the pore size distribution. The specific surface area and pore volume are listed in the table below. All tests are based on the total mass of the whole electrode.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m$^2$ g$^{-1}$)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>2.938</td>
<td>0.0065</td>
</tr>
<tr>
<td>Ni (oxidized)</td>
<td>3.236</td>
<td>0.0074</td>
</tr>
<tr>
<td>NiO/Ni</td>
<td>6.911</td>
<td>0.0161</td>
</tr>
<tr>
<td>RuO$_2$/NiO</td>
<td>5.923</td>
<td>0.0126</td>
</tr>
</tbody>
</table>

For the pristine Ni foam, no mesoporous structure can be observed. Even after the heat treatment in air, the increase in the specific surface area is limited. Interestingly, after the fabrication of NiO nanosheets, the specific surface area of NiO/Ni is largely increased, and a mesoporous structure appears, which is consistent with the TEM results in Fig. S3. After the decoration of RuO$_2$, the specific surface area of RuO$_2$/NiO electrode decreases, which may be caused by the dense RuO$_2$. But its pore distribution is similar as that of NiO/Ni electrode, indicating that the mesoporous structure of NiO nanosheets maintains.
Figure S5 EDS mapping of the RuO$_2$/NiO electrode: (a) shows the SEM image of the RuO$_2$/NiO electrode; (b-d) shows the corresponding element distribution of Ni, O, and Ru, respectively.
Figure S6 FTIR spectra of the discharged RuO$_2$/NiO electrode (blue line) in carbonate-based electrolyte (washed by pure TEGDME) in wavenumber ranges of 400-2000 cm$^{-1}$. Referring to the FTIR absorption peaks of the references (black lines), the discharged electrode contains Li$_2$CO$_3$, HCOOLi, CH$_3$COOLi, and LiOH (marked as the shaded areas) while there is no clear evidence of Li$_2$O$_2$ [2].
Figure S7 EDS mapping of the discharged RuO$_2$/NiO electrode in carbonate-based electrolyte: (a) shows the SEM image of the discharged RuO$_2$/NiO electrode, on which surface some product particles are formed; (b-e) shows the corresponding element distribution of Ni, C, Ru, and O, respectively. Note that the liquid TEGDME is completely dried during the SEM operation, so that C element comes from the discharge products. As shown in (b), (c), and (e), the positions of product particles are absence of Ni element but with C and O elements, indicating that the product particles are covered the electrode surface and composed of carbonate species.
Figure S8 LSV curves of (a) NiO/Ni and (b) RuO$_2$/Ni electrode of blank and pre-filled with LiOH and Li$_2$CO$_3$ in 1.0 M LiTFSI/TEGDME at a sweep rate of 1 mV s$^{-1}$. For the NiO/Ni electrode pre-filled with Li$_2$CO$_3$, the onset potential is 3.52 V, which is close to the result of the RuO$_2$/NiO electrode (3.56 V). Interesting, the electrode pre-filled with LiOH also presents an onset potential of 3.60 V, suggesting that the NiO/Ni electrode also has activities in the decomposition of LiOH. For the RuO$_2$/Ni electrode pre-filled with LiOH, the onset potential is 3.31 V, identical to the RuO$_2$/NiO electrode, and the current density is higher than that of the NiO/Ni electrode. The results indicate the electrocatalytic activity of RuO$_2$ in the LiOH decomposition. Beside, for the electrode pre-filled with Li$_2$CO$_3$, an onset potential of 3.53 V is also presented, close to that of the NiO/Ni electrode. This may be caused by the existent of NiO, which is formed during the fabrication process of RuO$_2$/Ni electrode (Fig. S2).
Figure S9 Discharge and charge curves of the RuO$_2$/NiO cathode in the argon and oxygen atmosphere with the pressure of 1.0 atm. At the Ar atmosphere, the discharge capacity is only 34 mAh g$^{-1}$, which is about 1.1% of the capacity (3240 mAh g$^{-1}$) obtained at O$_2$ atmosphere. Hence, the discharge capacity delivered at O$_2$ comes from the oxygen reduction reaction, rather than the reduction of RuO$_2$ [3, 4].
Figure S10 Comparison in the discharge-charge profiles between the RuO$_2$/NiO and RuO$_2$/Ni cathodes tested in oxygen at the same current density.
Figure S11 Discharge and charge curves of the RuO$_2$/NiO cathode with different loadings of RuO$_2$. With the loading increasing from 0.05 to 0.08 and 0.18 mg cm$^{-2}$, the specific capacity decreases from 3240 to 2725 and 2125 mAh g$^{-1}$, respectively. Hence, an increase in the catalyst loading can lead to a decrease in its utilization, which agrees with the reported results [5, 6].
Figure S12 Photograph of (a) separator and (b) lithium anode after 50 cycles.
Figure S13 Cycling stability test of the RuO$_2$/NiO cathode (after 50 cycles) in a rebuilt lithium-oxygen battery at the current density of (a) 250 mA g$^{-1}$ and (b) 500 mA g$^{-1}$ with a fixed capacity of 500 mAh g$^{-1}$: (1) Discharge-charge profiles of selected cycles; (2) Terminal discharge and charge voltages and energy efficiency.
**Figure S14** Comparison in the discharge-charge profiles between different cathodes tested in ambient air at the same current density. The results presented in Fig. S14 show a capacity of 1.1 µAh cm\(^{-2}\) with the Ni cathode, while a capacity of 0.009 mAh cm\(^{-2}\) with the NiO/Ni cathode. However, with the addition of RuO\(_2\), the discharge capacity is much improved (RuO\(_2\)/Ni: 0.063 mAh cm\(^{-2}\), RuO\(_2\)/NiO: 0.173 mAh cm\(^{-2}\)).
Figure S15 (a) Charge and discharge voltage profiles of the LiFePO$_4$-Li battery with the electrolyte of 1.0 M LiTFSI/TEGDME. The charge and discharge voltage of a LiFePO$_4$-air battery is converted to the voltage versus Li/Li$^+$ using the value of 3.430 and 3.448 V, respectively. (b) To verify the validation of the voltage conversion, a battery with a LiFePO$_4$ anode was discharged and charged under pure oxygen at the current density of 250 mA g$^{-1}$, and the converted voltage profiles were compared with those of a battery with a lithium anode, which shows good consistence.
References


