

Supporting Information

In-situ constructing a continuous ionic conductive coating for high-performance Li_3VO_4 anode

Lulu Wang,^{‡a} Ceng Zheng,^{‡a} Jianing Liang,^a Chun Zhai,^{*b} Hao Liu,^c Tianyou Zhai^a and Huiqiao Li^{*a,d}

^a State Key Laboratory of Materials Processing and Die and Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.

E-mail: hqli@hust.edu.cn

^b School of Materials Engineering, Changshu Institute of Technology; No.99 South Third Ring Road (Donghu Campus), Changshu 215500, Jiangsu, China. E-mail: zczhaichun@clsg.edu.cn

^c Centre for Clean Energy Technology, Faculty of Science, University of Technology Sydney, Broadway, Sydney, NSW 2007, Australia.

^d Shenzhen Research Institute of Huazhong University of Science and Technology, Shenzhen 518063, China

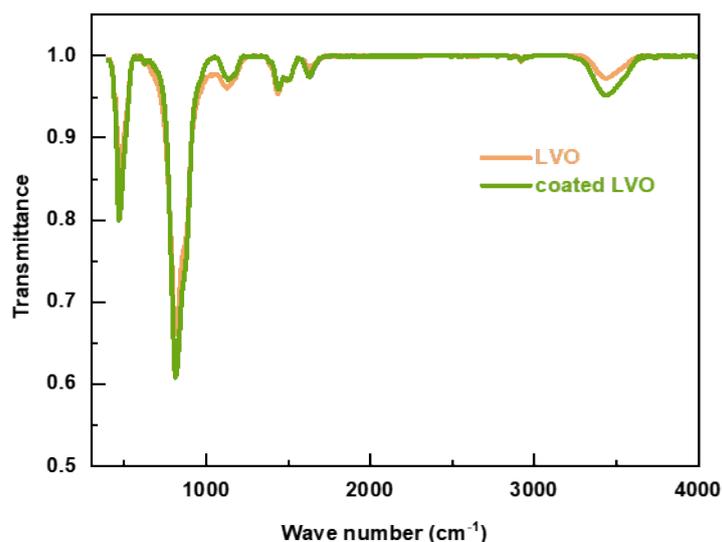


Figure S1. Infrared spectrum of pristine LVO and coated LVO-80.

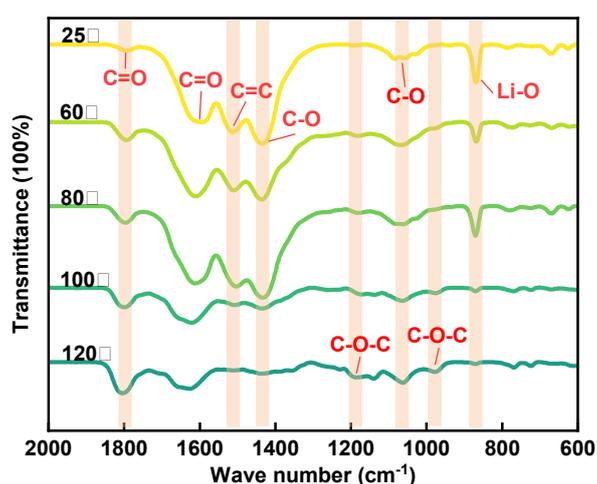


Figure S2. Infrared spectrum of polymerization product at different temperature.

The infrared spectra illustrated the changes of polymerization products' composition at different temperature. Referring to the infrared characteristic absorption peaks of the polymerization reaction products in Table S1, the characteristic peaks at 1794, 1064, 1180, and 977 cm^{-1} are attributed to C=O, C-O, and C-O-C bonds in polycarbonates, respectively. The peaks of 1597 and 1433 cm^{-1} are attributed to C=O and C-O bonds in alkyl lithium carbonate; The peak of 866 cm^{-1} is attributed to Li-O bonds in alkyl lithium oxygens or lithium carbonate; The characteristic peak at 1514 cm^{-1} is attributed to the C=C bond in the carbonate and the rest of the peaks are from the methyl and methylene chains. When the temperature of the polymerization reaction was at 25-80°C, the resulting products contain C=O, C-O, Li-O, and C=C bonds. These bonds are attributed to alkyl

lithium carbonate, lithium oxide, lithium carbonate, and carbonate after ring opening, respectively. all of these products belong to a group of small inorganic molecules, thus the coating layer on the surface of LVO seem like comprised with nanoparticles (Figure3b, c). And it can be inferred that the polymerization reaction at 25-80 °C mainly occurs as a ring-opening reaction of the carbonate, followed by reaction of the ring-opened carbonate with a small portion of Li^+ . As the temperature increased to above 100°C, the C=C bond peaks vanished from the products, while the intensity of the C=O bond peaks rose, and new C-O-C bonds appeared, indicating that the products at this time were polycarbonate and lithium alkyl carbonate. It is hypothesized that as the temperature rises, the opened carbonate ring would self-polymerize and react with Li^+ present in the solution. And at this time, the coating layer is no longer presented as an accumulation of small particles (Figure3d, e). Therefore, the composition of the polymerization products varies at different temperatures.

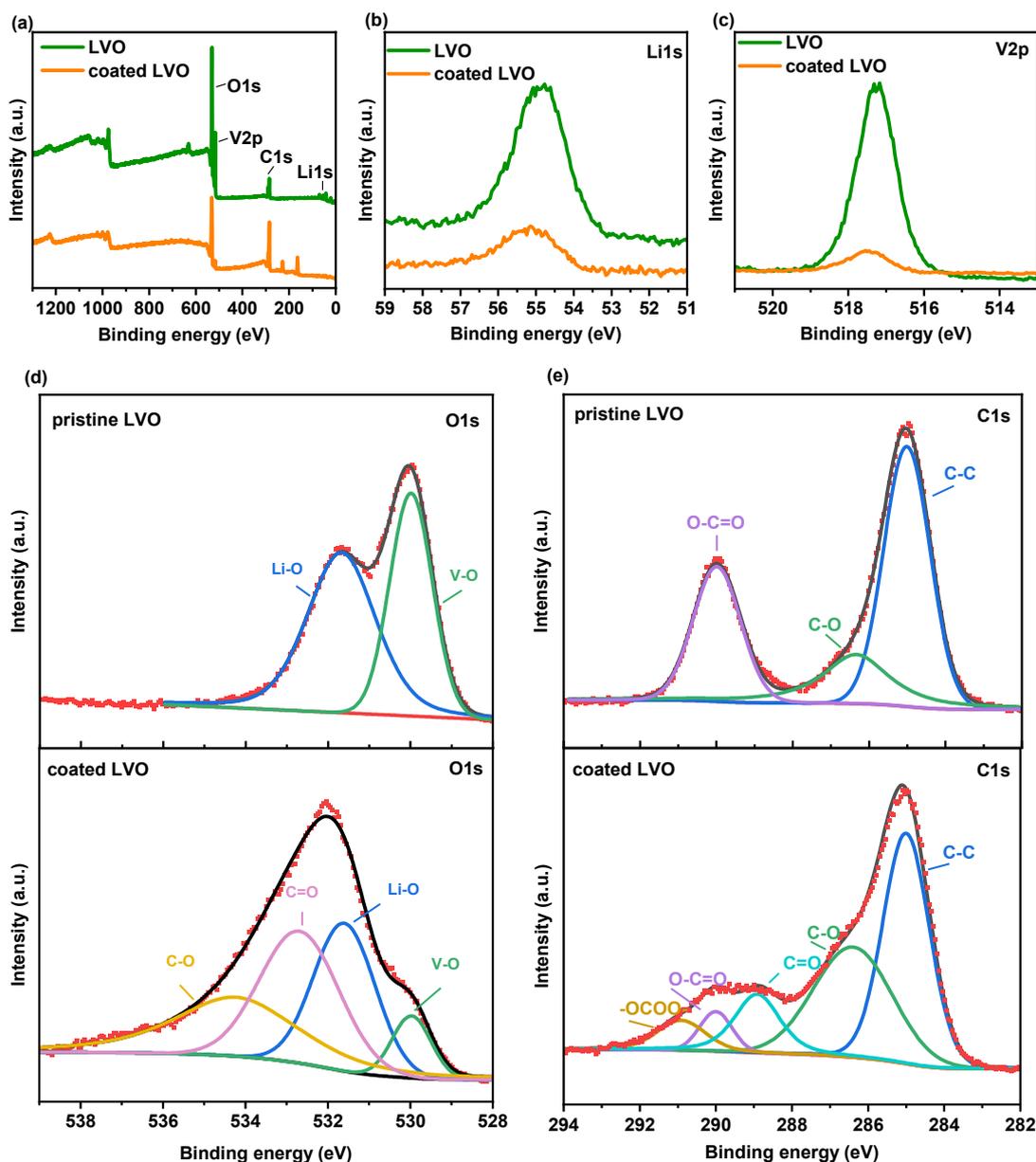


Figure S3. XPS surveys of pristine and coated LVO(a), Li 1s(b), V2p(c); XPS O1s spectrum of pristine(d) and coated LVO(e); XPS C1s spectrum of pristine(f) and coated LVO(g).

We used XPS to characterize the compositional changes on the sample surface before and after coating. The full spectra of LVO and coated LVO show the presence of Li, V, O, and C in the samples (4a). The intensity of Li1s peak(4b) at 55.15eV and V2p peak (4c) at 517.55eV decreased after coating, indicating that the contents of Li and V elements on the surface of the sample decreased after coating. This also proves the existence of a surface coating layer. We fitted the O1s peaks of the LVO powder as shown in Fig. 4d, and the peaks at 530.2 eV and 532.1 eV are derived from the V-O and Li-O bonds. Compared with the O1s peak of the LVO powder, the O1s peak of

the coated LVO powder (Fig. 4e) has two more peaks at 534.14 eV and 532.72 eV, which correspond to the peaks of the C-O and R-O-Li bonds, respectively. Similarly, as shown in Figure 4f, the C1s peak of the LVO powder was fitted, in which the peaks at 285eV, 286.4eV, and 290.2eV were derived from the bend of C-C, the C-O, and the O-C=O. The C1s peak of the coated LVO powder has two more peaks at 288.72eV and 291eV, corresponding to the ROCOOLi and -OCOO- bonds, respectively. In summary, compared to the pristine LVO powder, the increased peaks of coated LVO correspond to RO-Li, Li_2CO_3 , ROCOOLi, and polycarbonate of the coating layer, which is accord with the Infrared spectrum results of Figure 2e in the submitted manuscript.

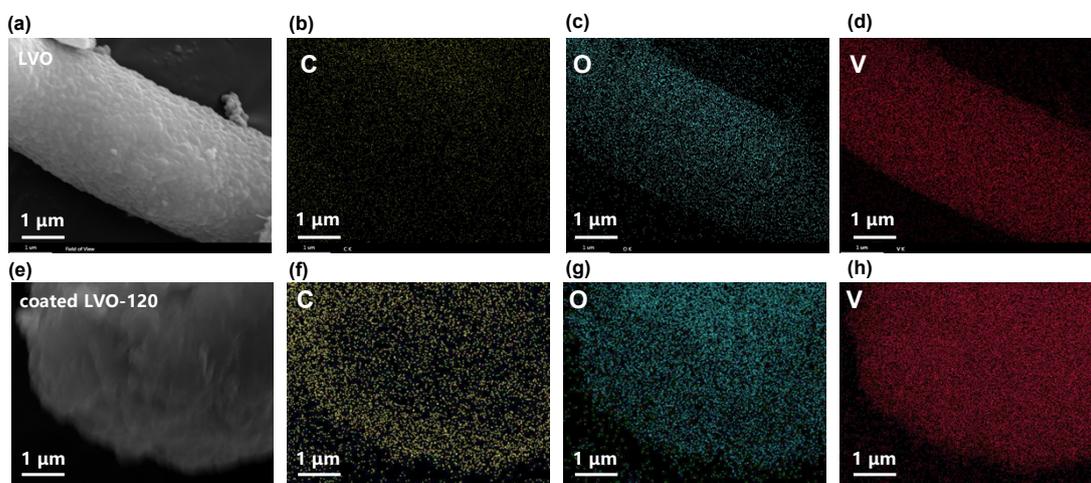


Figure S4. EDX mapping images of pristine LVO (a, b, c, d) and coated LVO-120 particle (e, f, g, h).

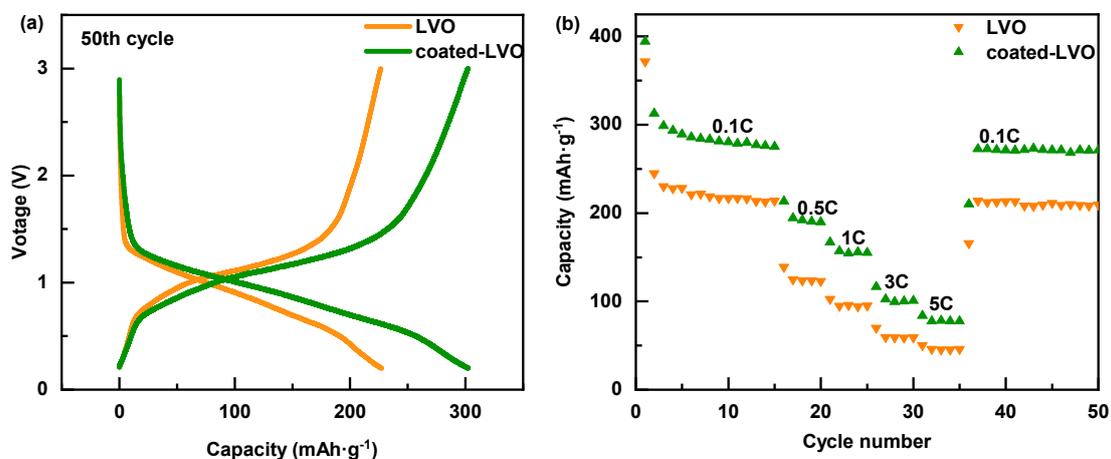


Figure S5. Typical charge-discharge curve of LVO and coated LVO at 50th cycle; rate performance of LVO and coated LVO-80.

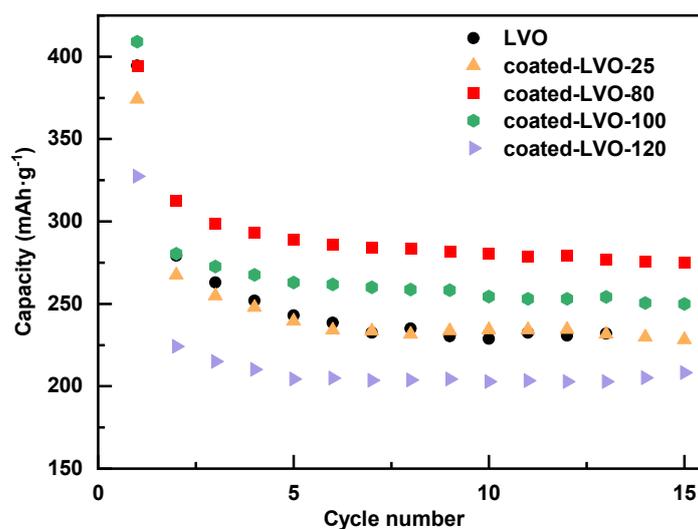


Figure S6. Cycle performance of pristine LVO and coated LVO-25, 80, 100, 120.

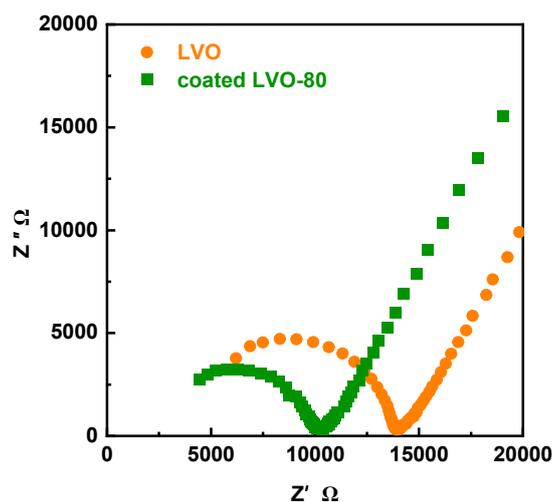


Figure S7. Electrochemical impedance spectroscopy for coated LVO-80 and pristine LVO.

The ionic conductivity tests were conducted on the pristine LVO powders and coated LVO, the frequency of EIS ranged from 0.01 Hz to 106 Hz and the amplitude is 30 mV, and the results are shown in Figure R7. According to the formula for ionic conductivity ($\delta = d/RS$), the ionic conductivity of coated LVO-80 powder is $\delta_{\text{coated-LVO-80}} = 1.07 \times 10^{-5} \text{ S/cm}$, and the ionic conductivity of pristine LVO powder is $\delta_{\text{LVO}} = 8.4 \times 10^{-6} \text{ S/cm}$. It is obvious that the coated LVO has a higher ionic conductivity which means the coated LVO has better ionic transportation than the pristine LVO.

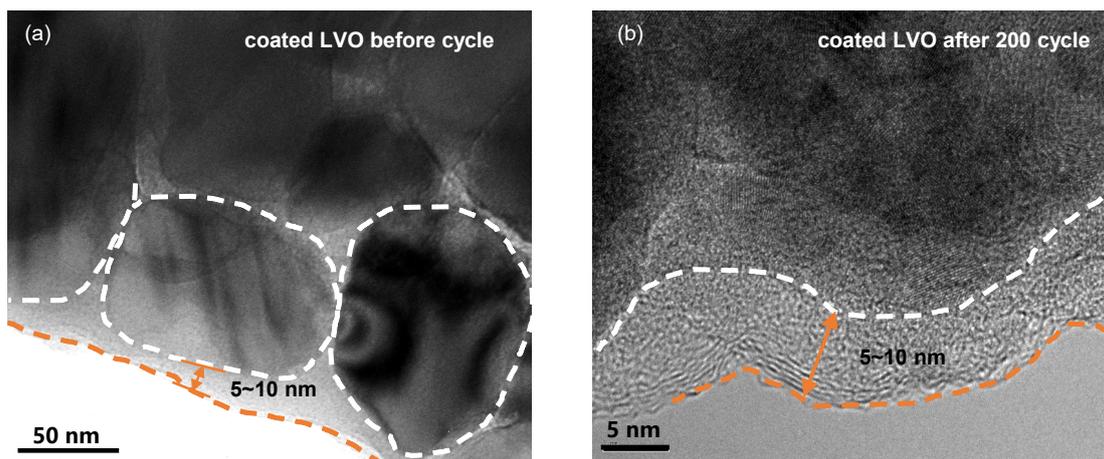


Figure S8. TEM images of coated LVO-80 before cycle(a) and after 200 cycles (b).

Table S1. Attribution of infrared characteristic absorption peaks of polymerization reaction products

Wave number(cm^{-1})	Mode of vibration	Assignment
1794	$\nu_{\text{C=O}}$	polycarbonate
1597	$\nu_{\text{C=O}}$	ROCOOLi
1514	$\nu_{\text{C=C}}$	Carbonate
1433	$\nu_{\text{C-O}}$	ROCOOLi
1180	$\nu_{\text{C-O-C}}$	polycarbonate
1064	$\nu_{\text{C-C}}$	polycarbonate
977	$\nu_{\text{C-O-C}}$	polycarbonate
869	$\delta_{\text{Li-O}}$	ROLi/ Li_2CO_3
775	$\beta_{\text{C-H}}$	$-\text{[CH}_2\text{]}_n-$
725	$\gamma_{\text{C-H}}$	$-\text{[CH}_2\text{]}_n-$