Supporting Information

CoV₂O₄ : A novel anode material for lithium-ion batteries with excellent electrochemical performance

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Experimental

Synthesis and method: Nano-porous CoV₂O₄ was synthesized using a solvothermal method. Typically, 0.8731 g of cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 98%, SHOWA) and 0.7019 g of Ammonium Vanadate (NH₄(VO₃), 99%, Alfa Aesar, 99%) were mixed in 40 mL methanol (CH₃OH, 99.9%, TEDIA) under stirring for 30 mins. Then, added 0.252 g of oxalic acid dihydrate (H₂C₂O₄·2H₂O, 99.5%, SIGMA-ALDRICH) to the solution and stirred for 1 hour. Dropwise 2.5 mL of nitric acid (HNO₃, 69.5%, Scharlau) and 2.5 mL of hydrogen peroxide (H₂O₂, 35%, SHOWA) to the solution and react 1 hour. Transfer the solution to a 100 mL Teflon-lined stainless steel autoclave and put in oven at 200 °C for 3 days then cooled to room temperature. The precipitate was washed with ethanol several times and dried at 80 °C. Afterward, the as-prepared precursor was calcined at 500°C for 8 h in H₂/N₂ atmosphere to obtain CoV₂O₄.

Electrochemical Tests: The electrochemical performance of the batteries were measured by CR2032 coin cells. The slurry composed of 80 wt.% active material, 10 wt.% Super P (Carbon black, 40 nm) and 10 wt.% binder that were polyvinylidene fluoride and CMC (carboxymethyl cellulose) + SBR (styrene-butadiene rubber, Asashi Chemical) were coated on to 10 µm copper foil which was used as the working electrode of the battery and the electrode was dried at 120 °C for 8 h in vacuum system to remove the residual water. The electrolyte consisted of 1.0 M LiPF₆ in ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1 in volume ratio). The charge/discharge test were analyzed using AcuTech System in the voltage range of 0.005 V and 3.5 V at room temperature. The mass loading of these sample was in the range of 1.16 - 1.42 mg/cm². The cyclic voltammograms (CV) were measured by CH Instruments Analyzer CHI 6273E at a

scan rate of 0.1 mV/s between 0.005 V and 3.5 V, then the AC impedance was tested in the frequency range from 0.01-100000 Hz.

	CoV2O4	ZnV ₂ O ₄
Space group	Cubic Fd-3 m	Cubic Fd-3 m
Lattice constant	a = b = c = 8.4030 Å	$a = b = c = 8.4111 \text{ \AA}$
Volume	593.345 Å ³	595.06 Å ³
R _p	6.43 %	
Rwp	8.33 %	
χ^2	1.949	

Table S1. Structural parameters of the Rietveld refined of as-prepare CoV_2O_4 and ZnV_2O_4 .



Fig. S1 (a)SEM image of CoV_2O_4 . EDS mapping of (b) O, (c) V and (d) Co and (e)TEM image, SAED pattern and (f) HRTEM of CoV_2O_4 .

Fig. S2 XPS wide scan (a), and XPS narrow scans of V 2p (b), Co 2p (c), and O 1s (d).

Fig. S3 dQ/dV profiles of CVO-P and CVO-C-S for 1^{st} cycle.

Fig. S4 dQ/dV profiles of (a) CVO-P and (b) CVO-C-S for 2nd, 50th and 100th cycle.

Fig. S5 Galvanostatic charge/discharge profiles of CVO-C-S electrode.

Figure S5 shows the galvanostatic charge/discharge profiles of CoV_2O_4 using CMC+SBR as the binders. Based on the theoretical capacity using 8 moles Li⁺ uptake, CoV_2O_4 should deliver about ~954 mAh·g⁻¹. The obtained initial discharge capacity is ~960 mAh·g⁻¹ which agrees well with the theoretical capacity. When CoV_2O_4 was fully discharged to 0.005V, its structure was destroyed with subsequent reduction of Co and V metals which are embedded onto the amorphous matrix of Li₂O and consumed 8 moles of Li⁺ ions. In the consequent discharge cycles, small humps at ~1.5 and ~0.6V are similar to the reduction peaks in the CV profiles. These peaks are considered to be the reduction of the metal oxides. Based on the initial charge, ~6 moles of Li⁺ were released upon charging to 3.5V as opposed to the theorized amount in equations 2-3. The initial coulombic efficiency is calculated to be ~74%. This relatively low coulombic efficiency could be primarily ascribed to the formed SEI layer. Subsequent charge profiles have peaks at ~1.25 and ~2.25V which are also similar to the oxidation peaks from the CV profile corresponding to the oxidation of Co and V metals. Moreover, the profiles of the 2nd and 3rd charge cycles are very similar to the 1st cycle.

Fig. S6 Cross section images of (a) fresh CVO electrode; (b) CVO-C-S and (c) CVO-P electrode after 100 cycles.

Fig. S7 (a) AC impedance and (b) diffusion coefficient of CVO-C-S and CVO-P electrodes.

Aside from cycling and rate capability tests, electrochemical impedance spectra (EIS) measurements of the electrodes were carried out to further prove the advantages of using CMC/SBR as binders. Fig. S7 shows the EIS impedance of the electrodes with the equivalent circuits. A typical EIS contains semicircles and a straight sloping line at the low frequency region.⁶² The internal resistance of the cell includes the combined resistance from the electrolyte, SEI, charge transfer, and Li⁺ ion diffusion into the electrode.⁶³⁻⁶⁶ In the inset of Fig. S7, measurements of R_s, R_{SEI} and R_{CT} are provided. R_s is known as the electrolyte resistance at the highest frequency. R_{SEI} and R_{CT} which are both in the middle frequency region, correspond to the resistance of the SEI film and charge transfer resistance, respectively. The sloping line (W, Warburg impedance) at the lower end of the frequency represents the diffusion of species. Since Rs and RsEI are of ohmic resistance, their combination is known as ohmic resistance, while RCT and W both reflect the kinetics of cell reactions, and when combined, is known as faradaic resistance.^{63,67} Based on the EIS plot, the R_{SEI} of CVO-C-S is smaller, and the R_{CT} semicircle is not very apparent which indicates smaller ohmic resistance and faradaic resistance than CVO-P. The measured R_s , R_{SEI} and R_{CT} of the CVO-C-S are 4.99, 41.54, and 10.44 Ω , respectively. Meanwhile, the calculated resistance for CVO-P electrode (obtained through fitting) are 5.03, 50.96, and 20.38 Ω . Furthermore, the diffusion kinetics were investigated by obtaining the Warburg coefficient, σ , through this equation:⁶⁸

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left(\frac{1}{C_{Li} D_{Li}^{0.5}} \right)$$
(1)

Where *R* is the ideal gas constant, *T* is temperature in Kelvin, *F* is the Faraday's constant, *A* is the electrode surface, C_{Li} is the concentration of Li in the electrolyte, and D_{Li} is the diffusion coefficient. By getting the slope (σ), the calculated D_{Li} for CVO-C-S and CVO-P electrodes are 1.42×10^{-13} and 6.06×10^{-14} cm²·s⁻¹, respectively. These values strongly demonstrate that both ionic diffusion and electron transport are faster in CVO-C-S electrode than CVO-P. This is believed to be due to the interconnected morphology of the electrode formed during the Li⁺ ions de/intercalation which provided ease of transport for the Li⁺ ions and electrons. Conversely, CVO-P suffered from cracks and volume expansion which increased both the ohmic and faradaic resistance of the cell.