Supporting Information

Tailoring the electrochemical properties of composite electrodes by introducing surface redox-active oxide film: VO_x-impregnated $LiFePO_4$ electrode

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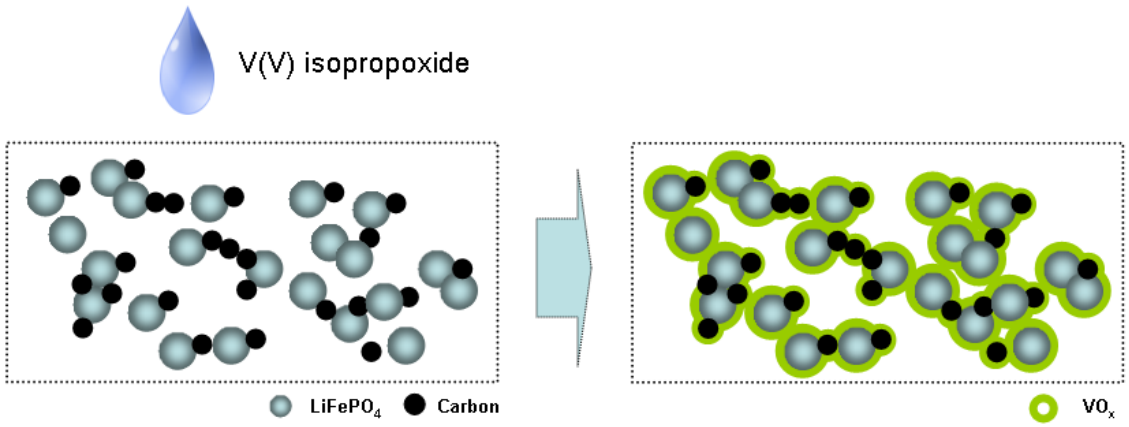
Experimental

$LiFePO_4$ powder synthesis

$LiFePO_4$ was synthesized by the conventional solid state reaction method. A stoichiometric amount of lithium carbonate, Li_2CO_3 (Wako, 99%), iron (II) oxalate dehydrate, $Fe(II)C_2O_4.2H_2O$ (Aldrich, 99%), and diammonium hydrogen phosphate, $(NH_4)_2HPO_4$ (Wako, 99%), were employed as starting materials. The mixture was thoroughly mixed and ground by a planetary milling apparatus (ITOH LA-PO4) for 24 hours. The sintering was conducted using a sealed tube furnace at 700 C for 6 hours under Ar gas flow to form $LiFePO_4$ without sacrificing purity.

Amorphous vanadium oxide impregnation into electrode composite

Vanadium oxide impregnated electrodes were prepared by the incipient wetness impregnation method in the Ar filled glove box. 0.02 mL vanadium isopropoxide solution in hexane (0.1 M concentration) was drop on to the porous $LiFePO_4$ electrode. After evaporating hexane from the electrode, the coating process was repeated several times to control the coating amount. For phase formation, the electrodes were aged in air and vacuum-dried before electrochemical tests.



Characterization

X-ray diffraction (XRD) analysis was performed using a Co Kα diffractometer (BRUKER AXS K. K., D8 ADVANCE) with Bragg Brentano geometry, and Rietveld refinement was carried out with TOPAS software. The electrode conductivity was checked with conventional 4 point probe method. The electrode composition for 4-point probe measurement is $LiFePO_4$:Carbon:PTFE=75:20:5 in weight and the impregnated VO_x is 5 wt.% of $LiFePO_4$. The X-ray photoelectron spectroscopy (XPS) analyses were performed with Φ PHYSICAL ELECTRONICS (QUANTUM 2000 SCANNING ESCA MICROPROBE) spectrometer using a focused monochromatized Al Kα radiation (1486.6 eV). The residual pressure inside the analysis chamber was 7×10^{-9} Torr. The core peaks were recorded with constant pass energy 29.9 eV. The XPS spectra were filled by using Multipak V6.1A software in which a Shirly background is assumed and the fitting peaks of the experimental spectra are defined by a combination of Gaussian (80%) and Lorentzian (20%) distributions.

For the electrochemical tests, the cathode slurry was coated on the aluminum foils and it was composed of 82 wt.% cathode active material, 10 wt.% carbon black, and 8 wt.% PVdF (polyvinylidene fluoride). The coin half cells using Li metal as counter electrode were assembled with the electrolyte, 1.3 M $LiPF_6$ in ethylene carbonate/diethylene carbonate (EC/DEC) 3/7 in volume. The coin cells were tested in the voltage range of 2.5 - 4.1 V vs. Li at room temperature, and the charging current density is fixed to C/5 during the rate capability test.

Table S1. Further Rietveld refinement results for Fig. 1

Atom	g	x	y	z	B / Å
Li	1	0	0	0	1.0
Fe	1	0.282339(10)	0.25	0.9734(3)	0.6
P	1	0.09505(17)	0.25	0.4166(4)	0.6
O1	1	0.0982(4)	0.25	0.7463(7)	1.0
O2	1	0.4530(5)	0.25	0.2102(5)	1.0
O3	1	0.1667(3)	0.0416(4)	0.2824(4)	1.0

Figure S1. Charge/discharge voltage curves of VO_x electrode at the rate of C/5. The electrode composition is VO_x:Carbon:PVdF=82:10:8 in weight.

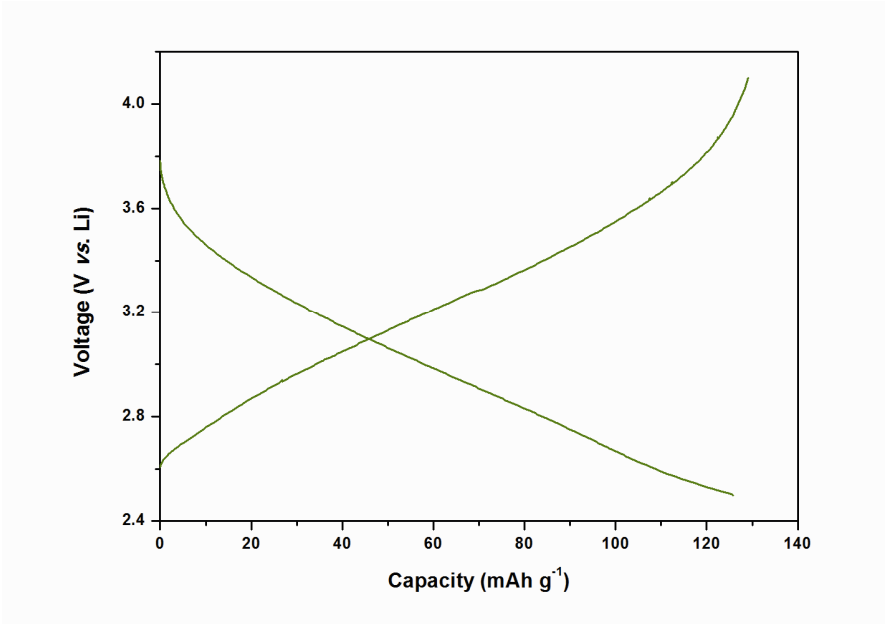
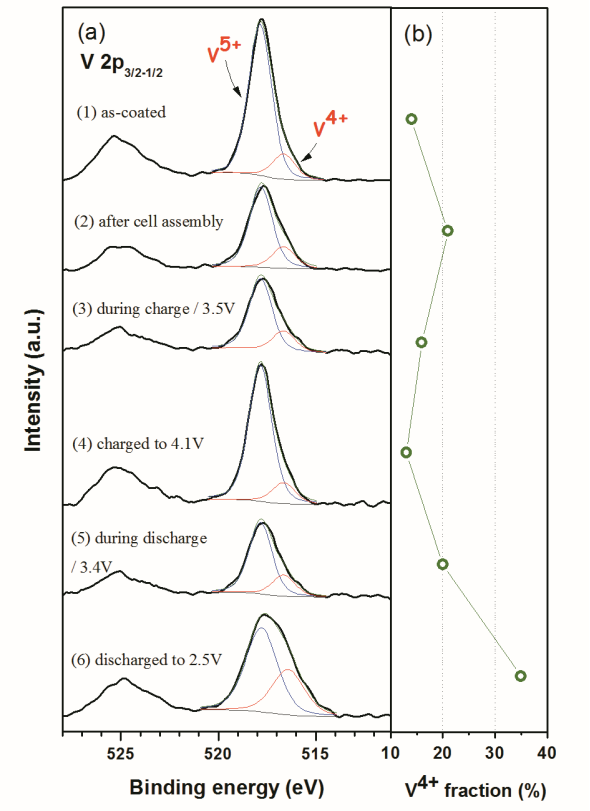


Figure S2. XPS (a) V $2p_{3/2\text{-}1/2}$ and (c) Fe $2p_{3/2\text{-}1/2}$ core peaks performed on as-coated and different stages of the initial charge (3.5, 4.1 V) and discharge (3.4, 2.5 V). The goodness-of-fitness values for V $2p_{3/2}$ fitted curves are presented in the table. (b) indicates the change of the relative percentage of V(IV) ions during the first charge/discharge cycle.



	(1)	(2)	(3)	(4)	(5)	(6)
Σχ2	2.33	2.3	2.29	2.45	1.46	1.68