Supporting Information

Delithiation/Lithiation Behaviors of Three Polymorphs of $LiVOPO_4$

Guang He,[a,b] Wang Hay Kan,[c] and Arumugam Manthiram*[a]

[a]*Materials Science and Engineering Program & Texas Materials Institute, The University of Texas at Austin, Austin, TX, 78712, USA*
[b]*Institute for New Energy Materials and Low-Carbon Technology, Tianjin University of Technology, Tianjin, 300384, P.R. China*
[c]*China Spallation Neutron Source, Institute of High Energy Physics, Dongguan, Guangdong, 523803, P.R. China*

Synthesis of α-$LiVOPO_4$ and β-$LiVOPO_4$: Both triclinic α-$LiVOPO_4$ and orthorhombic β-$LiVOPO_4$ were synthesized by a sol-gel process with some modifications.[18,19] α-$LiVOPO_4$ was prepared with $LiNO_3$ as the lithium source, V_2O_5 as the vanadium source, $NH_4H_2PO_4$ as the phosphate source, and citric acid as the chelator, while $LiNO_3$ and citric acid were replaced by lithium acetate and oxalic acid for the preparation of the β-$LiVOPO_4$. The resulting gels were calcined at 600 °C and 500 °C in air, respectively, for 10 h to obtain α-$LiVOPO_4$ and orthorhombic β-$LiVOPO_4$.

Synthesis of α_I-$LiVOPO_4$: Tetragonal α_I-$LiVOPO_4$ was synthesized by a microwave-assisted solvothermal (MT-SW) method.[35] Briefly, V_2O_5 was first dissolved in oxalic acid dehydrate (1:3) in deionized water at elevated temperatures. Next, $LiOH{\cdot}H_2O$, phosphoric acid (85%), and ethanol were added in sequence under stirring (V_{H2O}:V_{EtOH} = 1: 1). The V concentration was kept at 0.067 M, and Li:V:P = 1.8 : 1 : 1. The microwave reaction was allowed for ~ 50 min, including approximately 20 – 25 min of ramping time to the desired temperature/pressure. Finally, the products were collected and washed with water and acetone.

Synthesis of α-$LiVOPO_4$ nanoparticles: α-$LiVOPO_4$ nanoparticles were synthesized using ordered macroporous carbon as the hard template. The carbon was first prepared as described elsewhere.[38] Then, it was immersed into the precursor solutions to allow the penetration. α-$LiVOPO_4$ nanoparticles were formed after calcination in air, during which the carbon template was combusted in the furnace.

Chemical delithiation: Chemical delithiation was performed with three forms of $LiVOPO_4$ using nitronium tetrafluoroborate (NO_2BF_4) in the media of pre-dried acetonitrile in Ar atmosphere. For β- and α_I-$LiVOPO_4$, 50% excess (molar ratio) NO_2BF_4 was sufficient to produce pure β- and α_I-$VOPO_4$, while multiple delithiation was necessary for the complete delithiation of the α-$LiVOPO_4$. All the products were washed by acetonitrile twice after the reactions and kept in a vacuum oven at 150 °C for further use.

Chemical lithiation: Chemical lithiation was performed with three forms of $LiVOPO_4$ using n-butyllithium in pre-dried hexane under Ar atmosphere. Typically, ~ 5% excess n-butyllithium was added to ensure a complete lithiation. The reactions were allowed for 24 h, centrifuged with dry hexane twice, and stored in a glove box for further use.

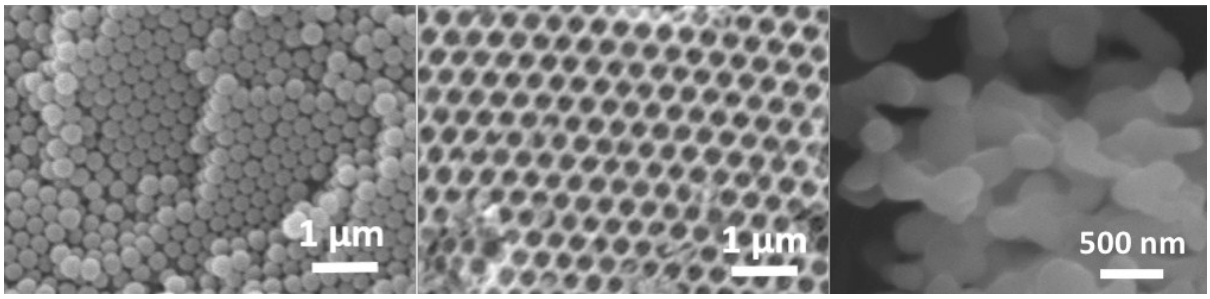

Figure S1 SEM images of poly(methyl methacrylate) spheres (left), the ordered macroporous carbon replica (middle), and the templated resulting α-$LiVOPO_4$ nanoparticles (right).

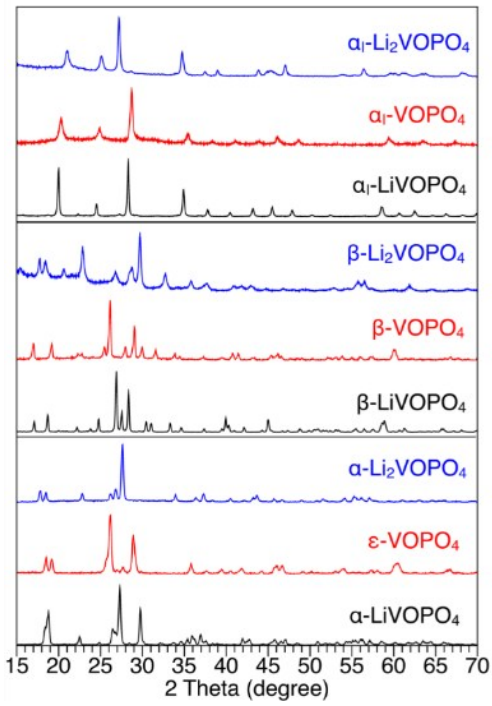

Figure S2 XRD patterns of the three $LiVOPO_4$ samples and the chemically delithiated $VOPO_4$ and chemically lithiated Li_2VOPO_4.

α-	**ICP (Li:V:P)**	**β-**	**ICP (Li:V:P)**	**α_I-**	**ICP (Li:V:P)**
α-$LiVOPO_4$	1.02:1.02:1	β-**$LiVOPO_4$**	1.03:0.99:1	**α_I-$LiVOPO_4$**	1.10:0.92:1
ε-$VOPO_4$	0.002:1.02:1	β-**$VOPO_4$**	0.03:0.98:1	**α_I-$VOPO_4$**	0.03:0.92:1
α-Li_2VOPO_4	2.04:1.02:1	β-**Li_2VOPO_4**	2.05:0.99:1	**α_I-Li_2VOPO_4**	2.07:0.93:1

Table S1 ICP results of three sets of $VOPO_4$-$LiVOPO_4$-Li_2VOPO_4 upon chemical delithiation and lithiation.

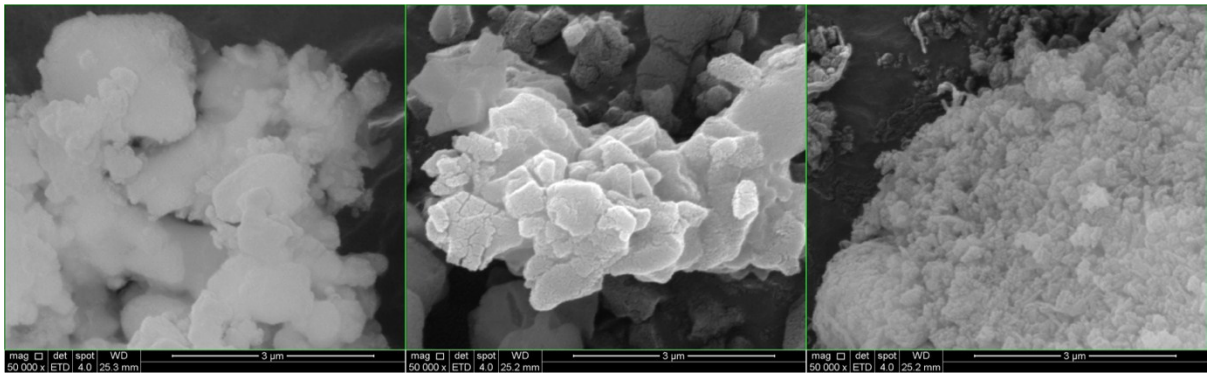

Figure S3 SEM images of α-$LiVOPO_4$ (left), β-$LiVOPO_4$ (middle), and α_I-$LiVOPO_4$ (right) upon chemical lithiation with n-butyllithium.

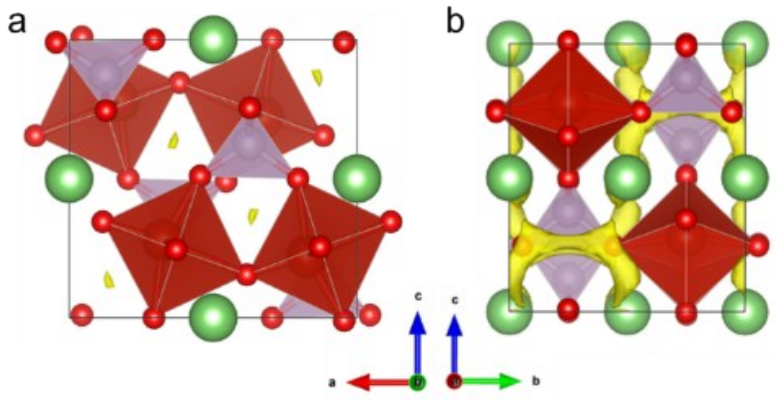

Figure S4. Bond valence sum (BVS) maps of β-$LiVOPO_4$, showing the possible positions of the 2nd Li in the lattice at mismatch of (a) 0.15 and (b) 0.20.

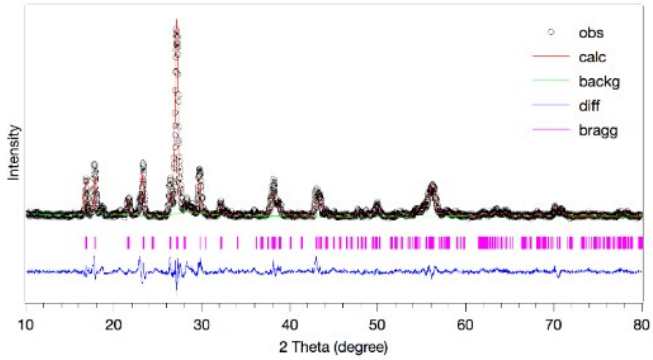

Figure S5. XRD pattern and Rietveld refinement of β-Li_2VOPO_4.

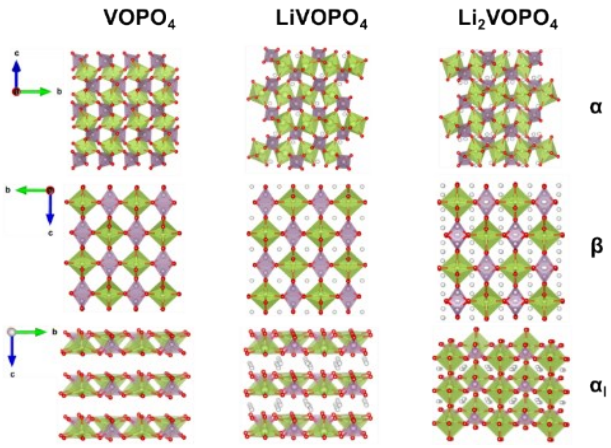

Figure S6. Crystal structures of three $VOPO_4$-$LiVOPO_4$-Li_2VOPO_4 systems. Note the structure of β-Li_2VOPO_4 is just the approximate illustration.