ε– and β-LiVOPO₄: Phase Transformation and Electrochemistry
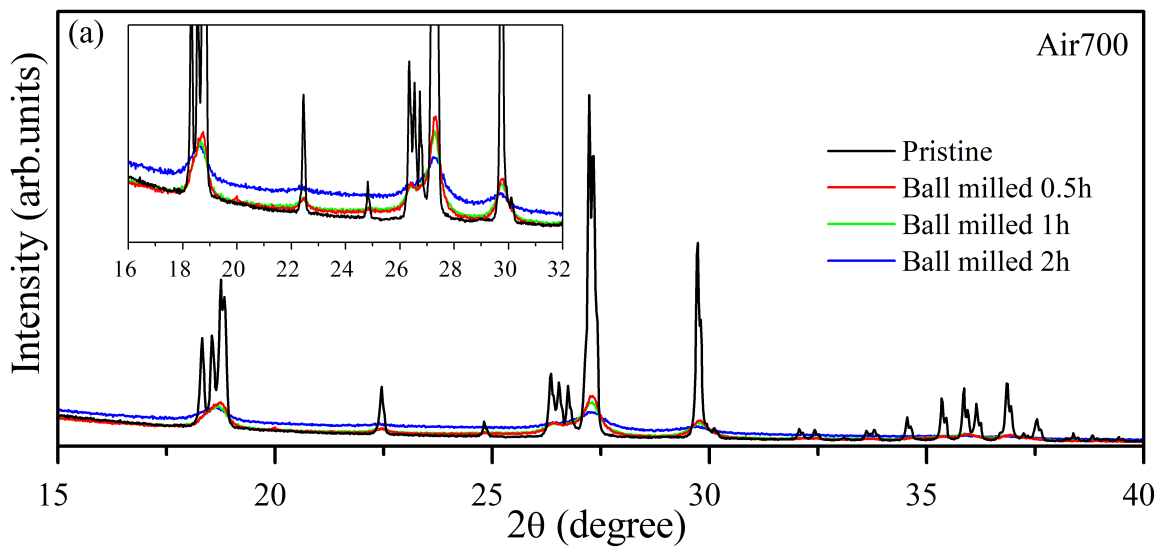
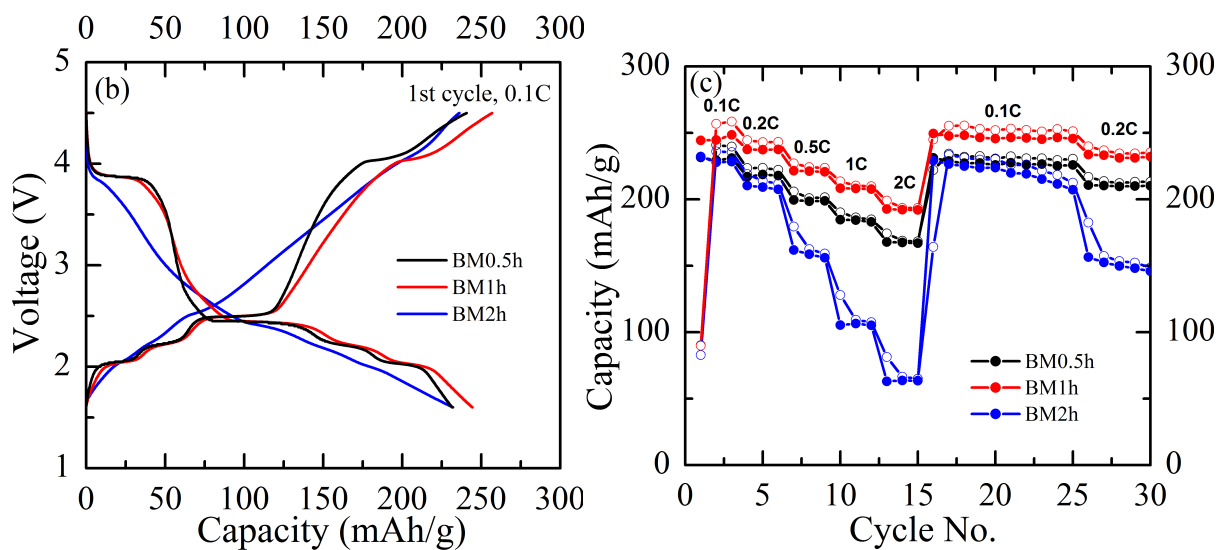*Hui Zhou[†], Yong Shi[†], Fengxia Xin[†], Fredrick Omenya[†], M. Stanley Whittingham[†, *]*

†Chemistry and Materials, Binghamton University, Binghamton, NY 13902-6000, USA
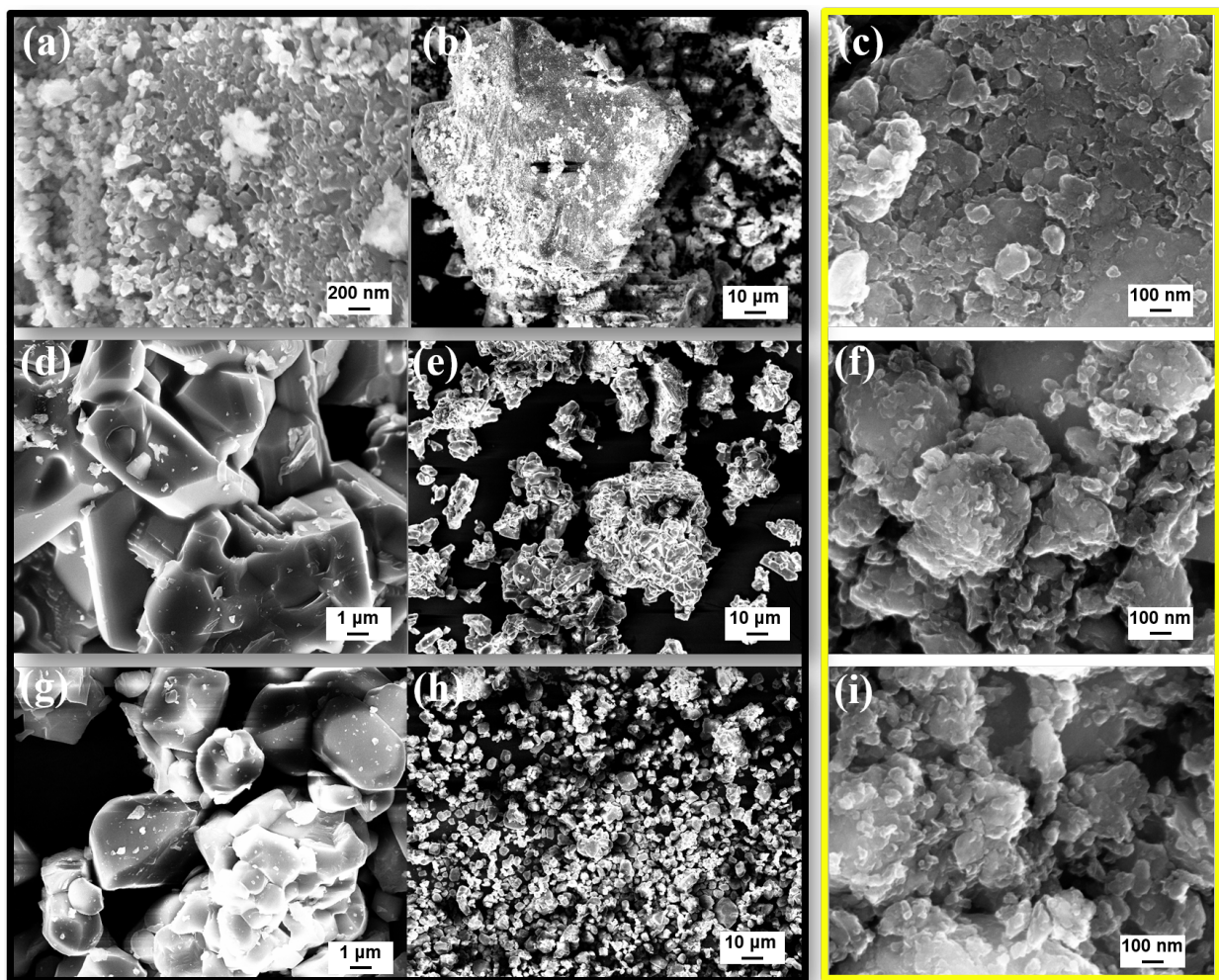
* stanwhit@gmail.com
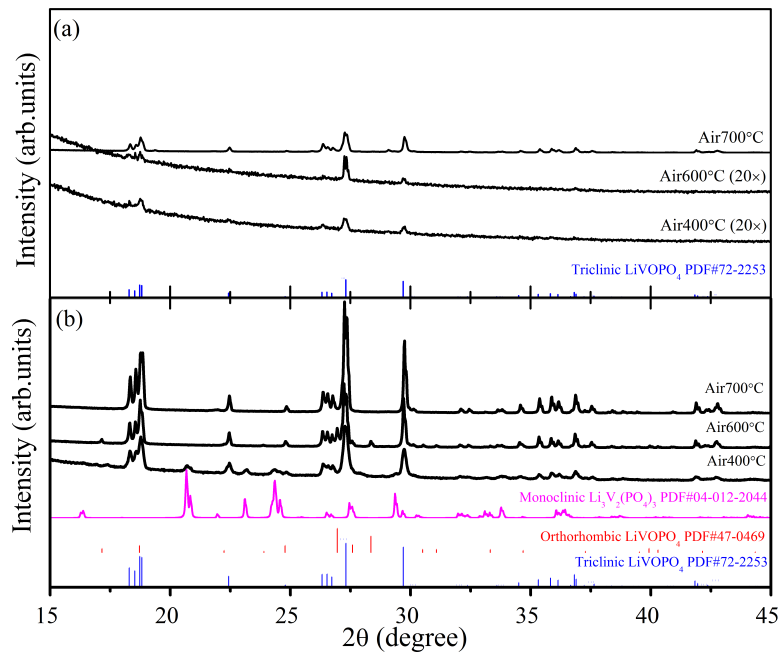
Figure S1. XRD patterns of the products after TG-MS measurements in (a) O_2 and (b) argon atmosphere for Air400, Air600 and Air700 samples.

Figure S2. Comparison of (a) XRD, (b) initial cycling profile, (c) rate property of Air700 sample

with different high-energy ball millings, where the cells were cycled in the voltage range of

1.6~4.5 V.

Figure S3. SEM pictures for Air400 ((a), (b) and (c)), Air600 ((d), (e) and (f)) and Air700 ((g), (h) and (i)) samples. (a), (b), (d), (e), (g) and (h) are for pristine materials; (c), (f) and (i) are for the samples after 1h ball milling with acetylene black. The morphology of the samples was observed by a field emission scanning electron microscope (SEM) (SUPRA 550 from Zeiss) at 15 kV.

Kinetics Study with Cyclic Voltammetry
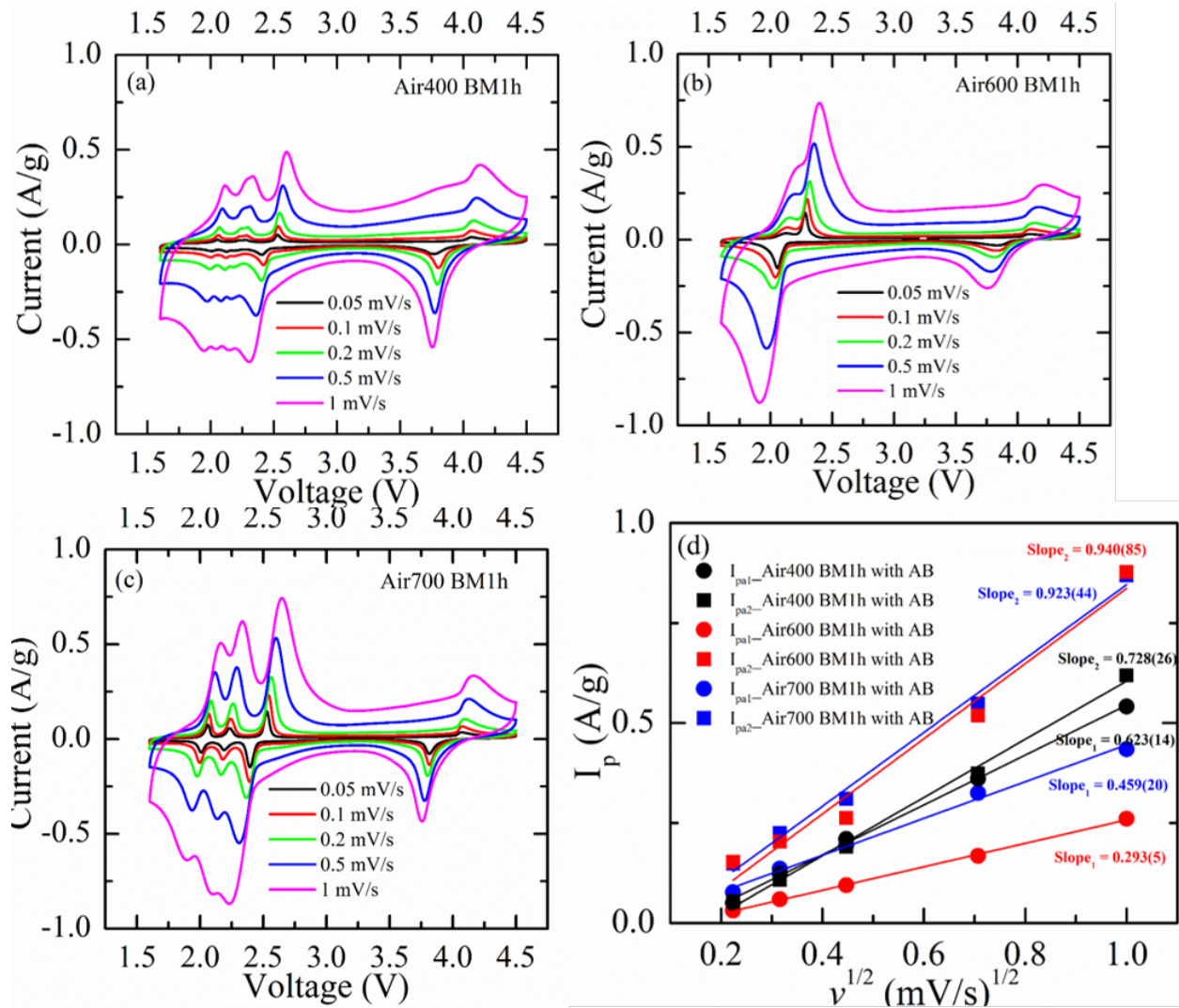
Figure S4. Cyclic voltammetry (CV) with different scan rates in the voltage range of 1.6 ~ 4.5 V for (a) Air400, (b) Air600 and (c) Air700 samples with 1h ball milling with acetylene black. (d) the corresponding plots of linear fit on I_p vs. $v^{1/2}$ for the first and second lithiatons (I_{pa1} and I_{pa2} represents the peak current of lithiation at high and low voltage respectively).

Fig. S4 compares the cyclic voltammetry (CV) of Air400, Air600 and Air700 with different scan rates. From Randles-Sevcik equation, at room temperature, the peak current of redox reaction in the CV can be described as:

$$i_p = 268600 n^{\frac{3}{2}} A D^{\frac{1}{2}} C v^{\frac{1}{2}}$$

5

i_p is the peak current in amps, n is the number of electrons transferred in the redox reaction, A is the electrode area in cm^2, D is diffusion coefficient in cm^2/s, C is the concentration in mol/cm^3 and v is the scan rate of CV in V/s. By varying the scan rate, a linear relationship between the i_p and $v^{1/2}$ can be obtained (Fig. S4d) and from the slope of the line, we can calculate the diffusion coefficient D of the sample. Considering the same composition and similar lattice volume for the three samples, combined with the same test conditions, the other parameters besides I_p and D, should be almost the same for all three samples. The diffusion coefficient D is proportional to the slope value, i.e., the larger the slope value, the higher the diffusion. Through comparison, the Air400 sample has the best diffusivity in the higher voltage plateau, but worst diffusivity in the lower voltage plateau; Air600 and Air700 sample have similar diffusivities in the lower voltage region, but Air700 has a little better diffusivity than Air600 in the higher voltage regime. This difference may be caused by the structural difference between the ε and β- LiVOPO$_4$.