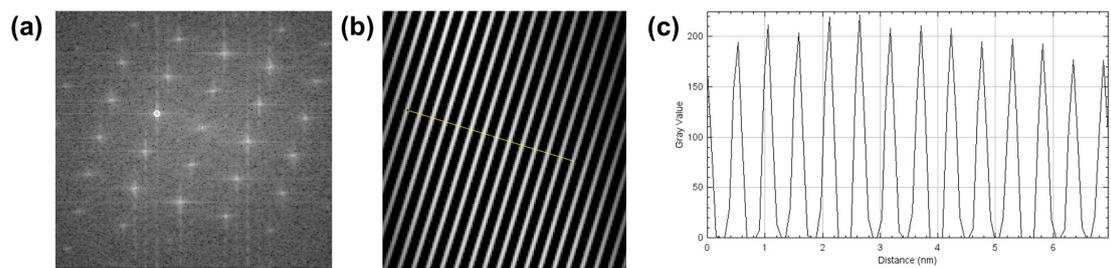


**Supplementary Information**

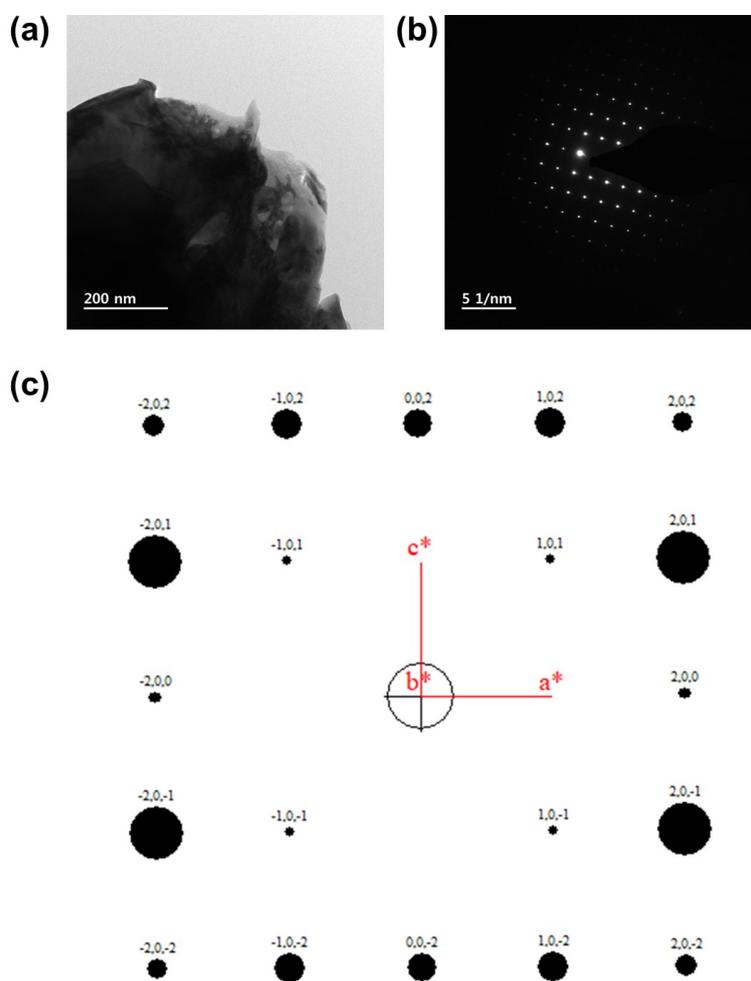
**Exploring the unexpected electrochemical dynamics of lithium  
vanadyl phosphate electrode in zinc battery system**

Dimas Yudianto Putro, Kiki Rezki Lestari, Muhammad Hilmy Alfaruqi, M. Ghalib Alfaza,  
Zulkifli, Moonsu Song, Seunggyeong Lee, Balaji Sambandam, Vinod Mathew, Jaekook Kim

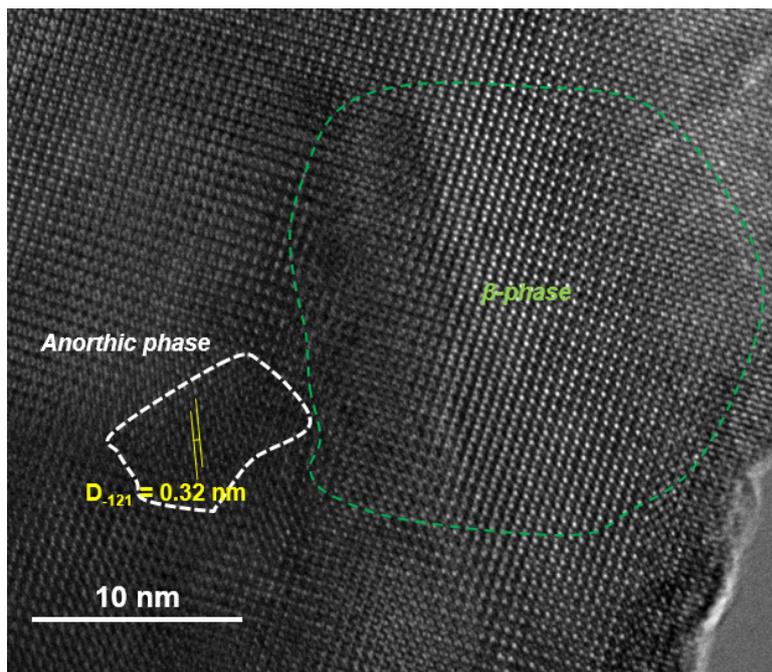
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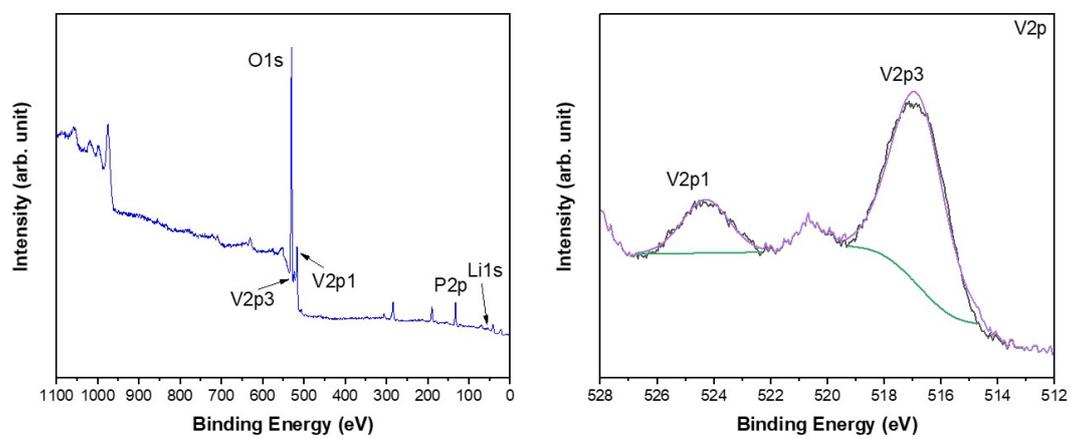
**Fig. S1** (a) FFT and (b) inverse FFT images analyzed using ImageJ. (c) The corresponding plot profile.



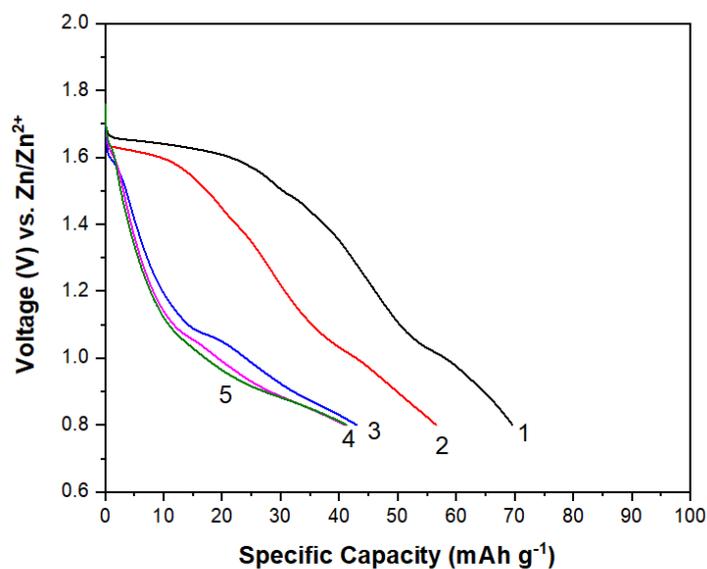
**Fig. S2** (a) TEM image of the powder, (b) corresponding selected area electron diffraction, and (c) reciprocal lattice indexed along [010] zone axis.



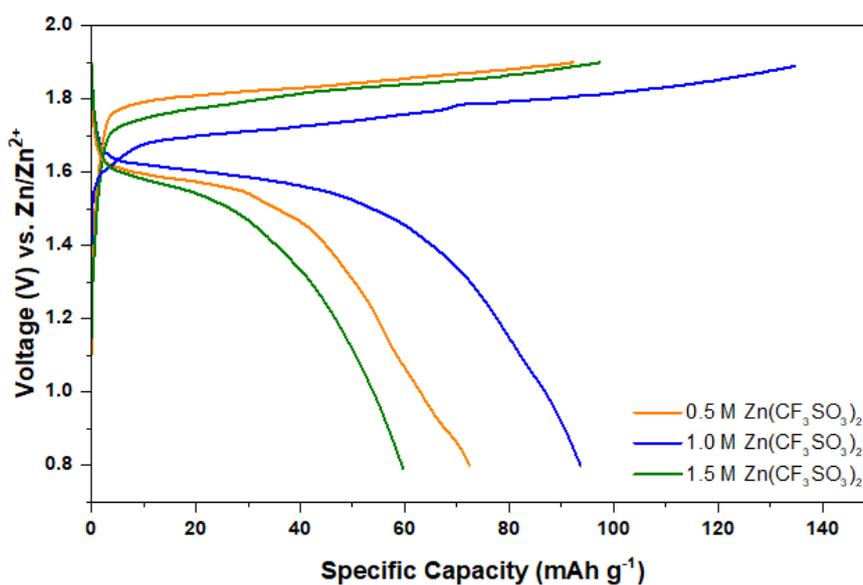
**Fig. S3** HR-TEM image of the sample.



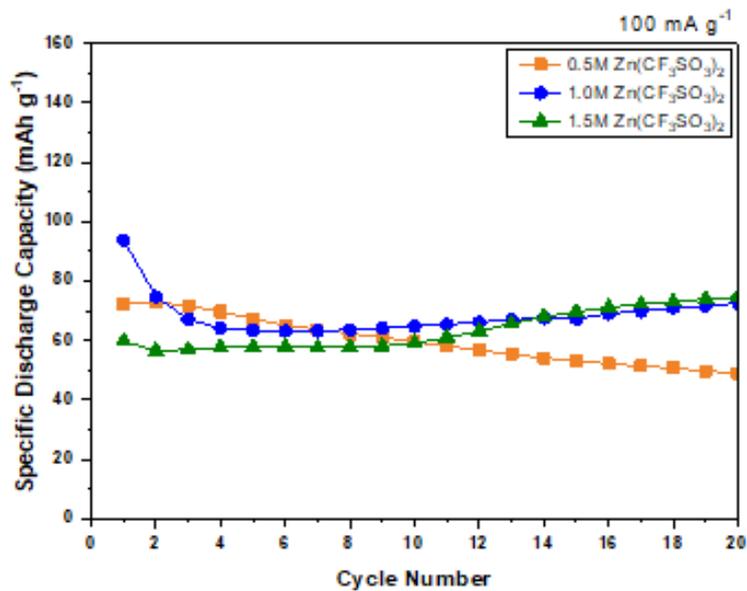
**Fig. S4** XPS spectrum of  $\beta$ -LiVOPO<sub>4</sub> sample.



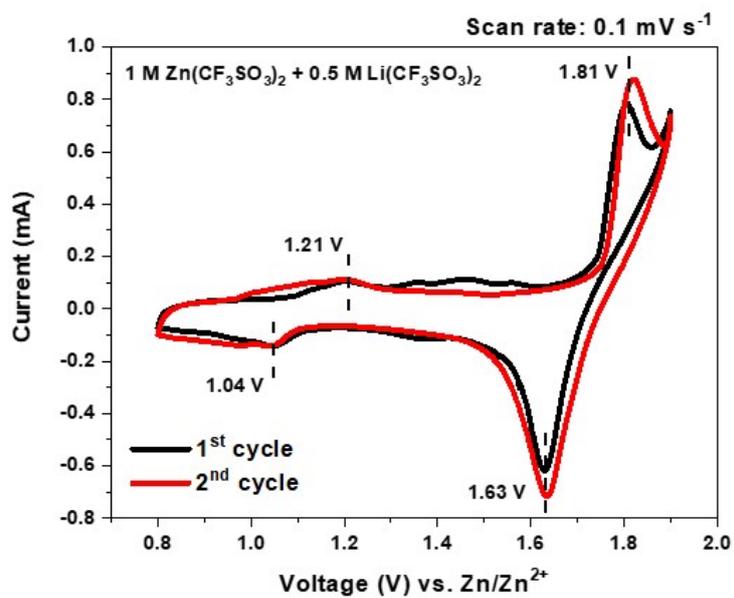
**Fig. S5** Electrochemical performance of  $\beta$ -LiVOPO<sub>4</sub> electrode using active material:conducting agent:binder ratio of 7:2:1.



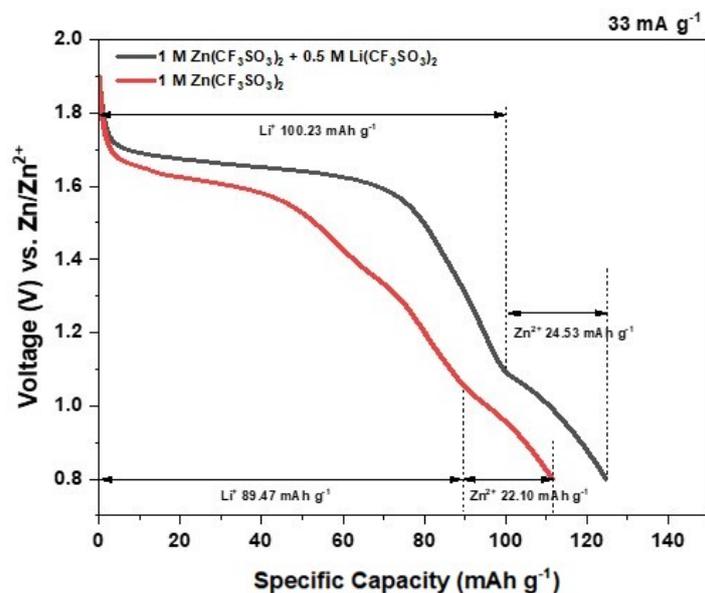
**Fig. S6** Initial voltage profiles of the Zn/ $\beta$ -LiVOPO<sub>4</sub> cells in different electrolyte concentrations cycled at a current density of 100 mA g<sup>-1</sup> within the potential window of 0.8 to 1.9 V.



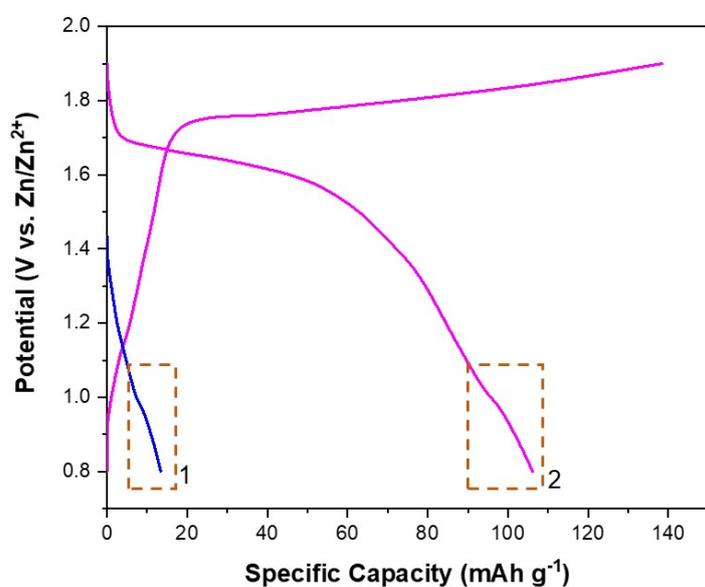
**Fig. S7** Cyclability test of the cathode using 0.5, 1.0, and 1.5 M Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> electrolyte.



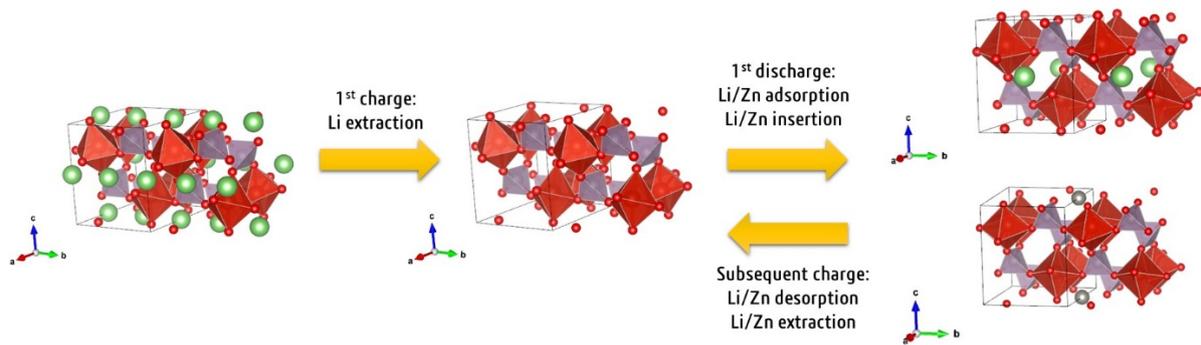
**Fig. S8** Cyclic voltammetry (CV) of  $\beta$ -LiVOPO<sub>4</sub> in a 1 M Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> + 0.5 M Li(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> electrolytes.



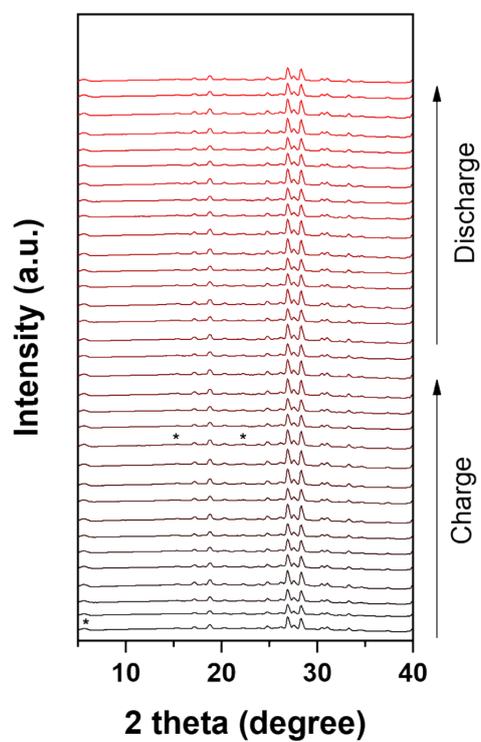
**Fig. S9** Comparison of electrochemical 1<sup>st</sup> discharge profiles of  $\beta$ -LiVOPO<sub>4</sub> in different electrolytes.



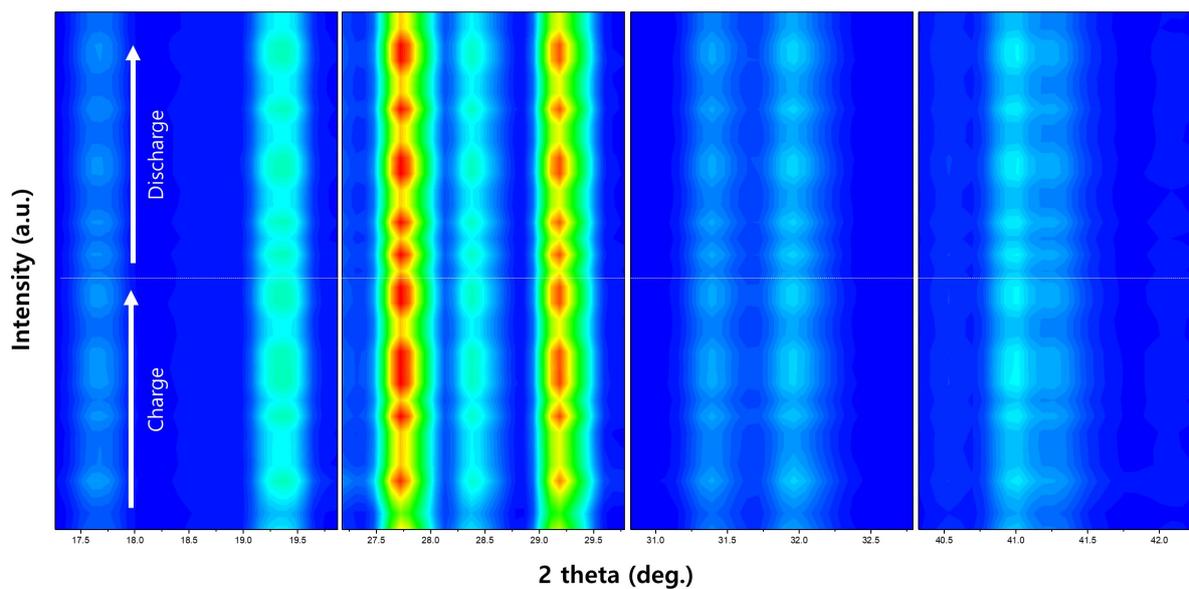
**Fig. S10** Initial voltage profiles of the Zn/ $\beta$ -LiVOPO<sub>4</sub> cells in 1 M Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> electrolyte cycled at a current density of 100 mA g<sup>-1</sup> within the potential window of 0.8 to 1.9 V. The cell was initially discharged.



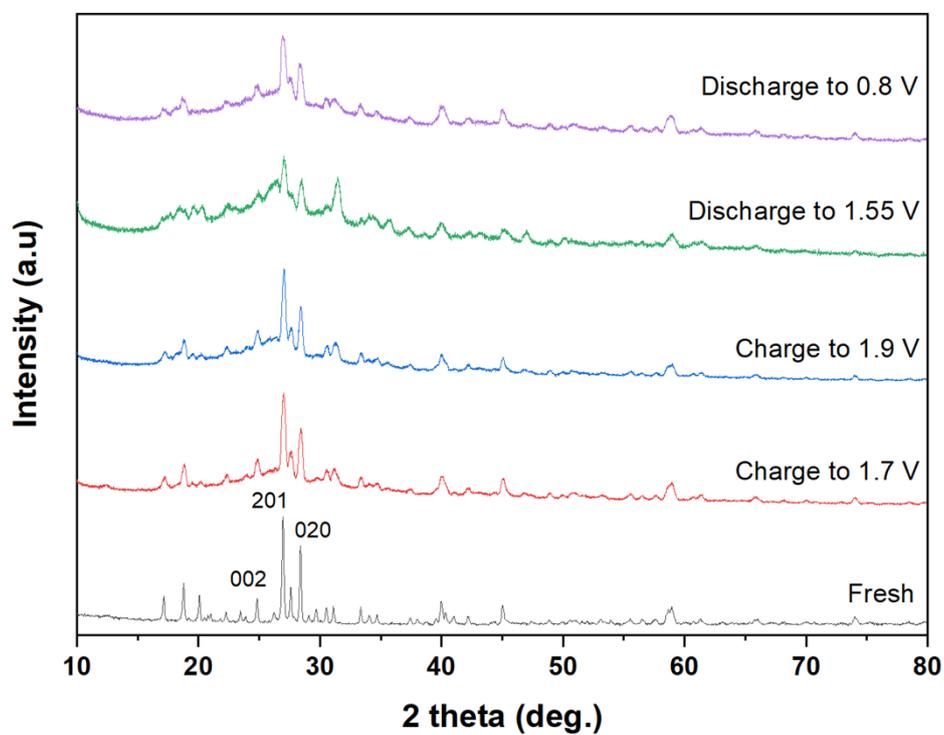
**Fig. S11** Proposed electrochemical mechanism of  $\beta$ -LiVOPO<sub>4</sub> cathode in the zinc cell.



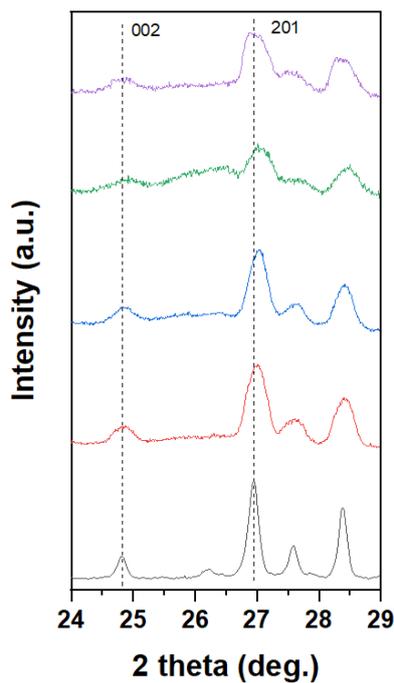
**Fig. S12** *In situ* SXR D patterns of the Zn/ $\beta$ -LiVOPO<sub>4</sub> cell taken during initial charge/discharge cycle.



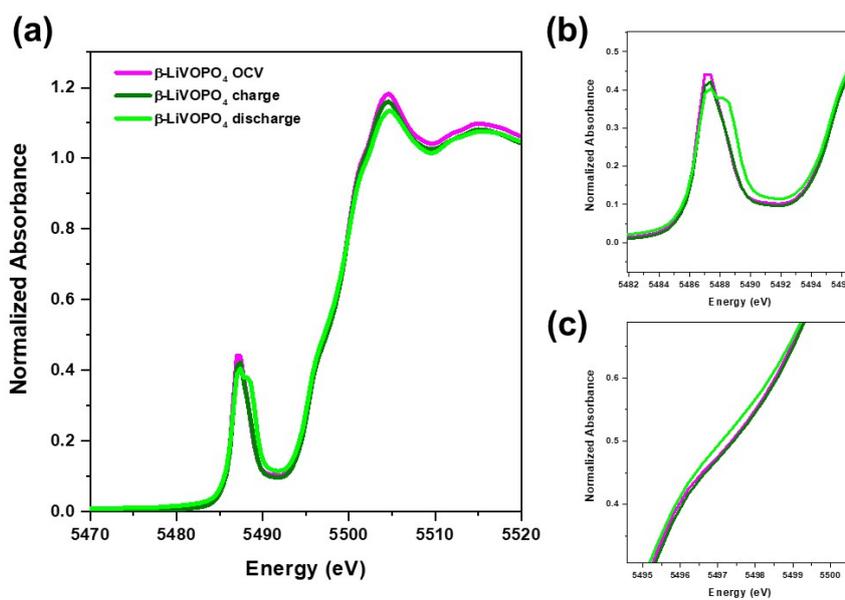
**Fig. S13** Magnified view of selected contour plots derived from *in situ* SXRD of the Zn/ $\beta$ -LiVOPO<sub>4</sub> cell obtained during initial charge/discharge cycle.



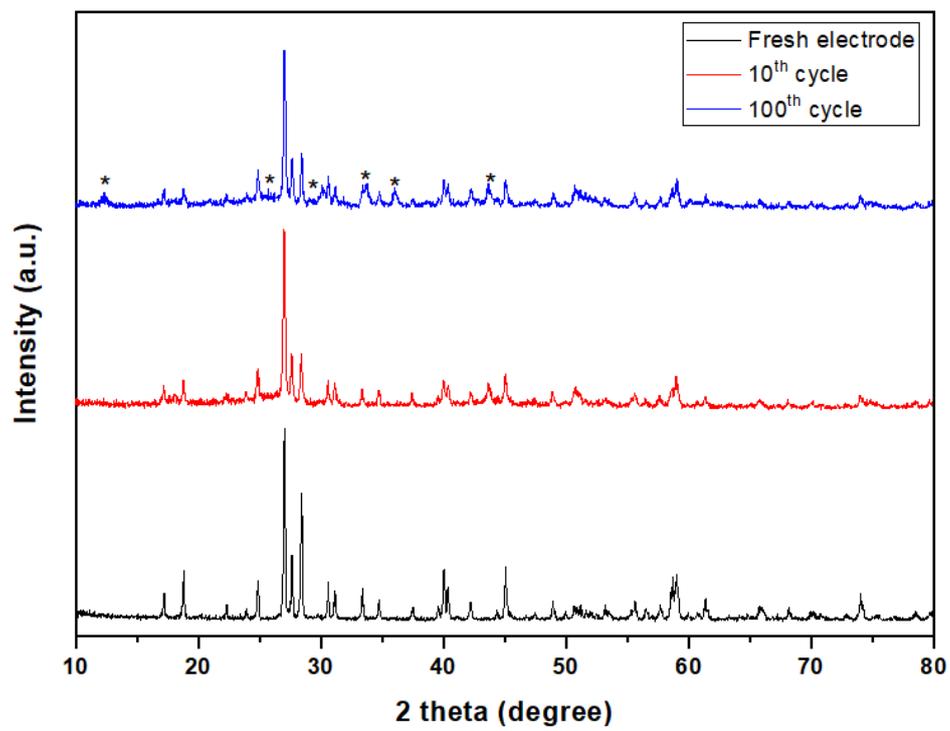
**Fig. S14** *Ex situ* XRD patterns of the cycled electrodes.



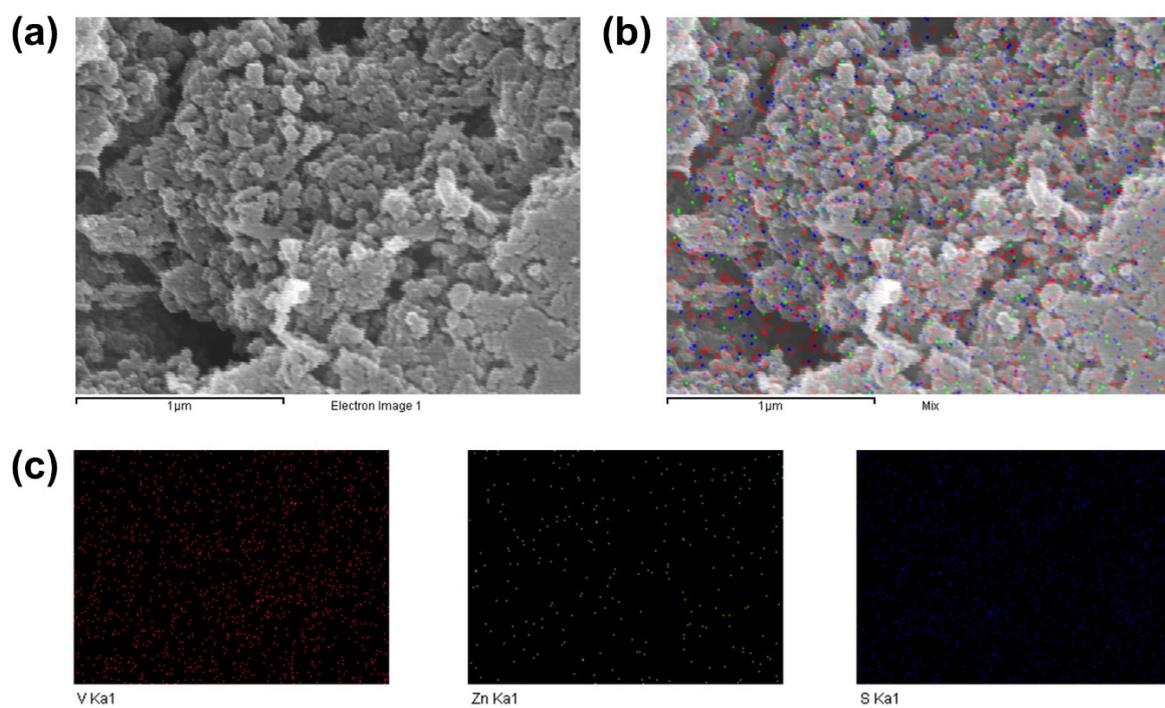
**Fig. S15** Magnified view of selected *ex situ* XRD patterns of the cycled electrodes derived from Fig. S14.



**Fig. S16** (a) *Ex-situ* V K-edge XANES spectra of the  $\beta$ -LiVOPO<sub>4</sub> OCV. Corresponding magnified (b) pre-edge and (c) main edge spectra.



**Fig. S17** *Ex situ* XRD of the electrodes after 10<sup>th</sup> and 100<sup>th</sup> discharge cycles.



**Fig. S18** *Ex situ* SEM and EDX mapping of the cycled electrode.

**Table S1** Electrolyte pH value in various concentration.

Electrolyte Concentration (M)	pH
0.5	5.92
1	5.56
1.5	5.24
2	4.85

**Table S2** *Ex-situ* ICP electrolyte after the initial charge and discharge cycles.

Electrolyte	Element	Concentration (ppm)
1 <sup>st</sup> charge	V	65
	Li	7.97
1 <sup>st</sup> discharge	V	21.80
	Li	5.90