Electrochemical Performance of Nanosized Disordered LiVOPO$_4$

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Figure S1. Rietveld refinement of XRD ($\lambda=1.54$ Å) for the as-synthesized LVPO by solid-state reaction. (space group: $P\bar{1}$, $a = 6.739$ Å, $b = 7.199$ Å, $c = 7.916$ Å, $\alpha = 89.83^\circ$, $\beta = 91.30^\circ$, $\gamma = 116.93^\circ$, $R_{wp} = 4.6\%$)

Table S1. Crystallite size and strain of pristine and ball-milled LVPO calculated by the Double-Voigt approach on TOPAS.

| Samples                  | $L_{Vol-IB}$ (nm) | $\varepsilon_0$   |
|--------------------------|-------------------|-------------------|
| Pristine LVPO            | 250 (11)          | 0.00026 (1)       |
| LVPO HEBM 0.2 h          | 187 (11)          | 0.00334 (1)       |
| LVPO HEBM 0.3 h          | 65 (1)            | 0.00336 (1)       |
| LVPO HEBM 0.4 h          | 58 (1)            | 0.00394 (2)       |
| LVPO HEBM 0.5 h          | 44 (3)            | 0.00489 (2)       |
| LVPO HEBM 0.6 h          | 31 (1)            | 0.00528 (2)       |
| LVPO HEBM 0.7 h          | 38 (1)            | 0.00525 (2)       |
EXAFS analysis:

A theoretical $\chi(k)$ function was generated by performing ab-initio calculations on relevant structural models using the code FEFF8.2,\textsuperscript{1} which was least-square fitted the data using the software ARTEMIS of the package IFEFFIT.\textsuperscript{2}

**Figure S2.** EXAFS fits to the data of ball milled $\varepsilon$-LiVOPO$_4$ samples.

**Figure S3.** Variation in the short vanadyl bond length and its distribution with ball milling time.
EXAFS data of the ball milled samples were explained based on the triclinic structure of LiVOPO$_4$ (space group: $P\overline{1}$). Typical fitting parameters involved an amplitude reduction factor $S_0^2$ and an overall energy parameter $\Delta E_0$ for each dataset in addition to a fractional change in the bond length, $\alpha$, and a mean-squared relative distribution parameter, $\sigma^2$, for each coordination shell depending on the type of backscattering atoms. Since V atoms are distributed over two distorted octahedral sites in triclinic LiVOPO$_4$, local structures around these two sites were averaged to fit the data. The first coordination shell around V has six oxygen atoms with short (1.626–1.627 Å), medium (1.945-2.099 Å) and long (2.240 Å) bond lengths. Best-fit to the data was achieved when separate fitting parameters were assigned to these bond lengths. A good agreement between the data and fit for all samples can be seen in Figure S2. The refined values of vanadyl bond length and its distribution are plotted against ball milling time in Figure S3. With increasing ball milling time, the short vanadyl bond length increases, which is consistent with reduction of V$^{4+}$ to V$^{3+}$ since the short vanadyl bond exists only for V$^{4+}$. For this reason and since V K-edge XAS in the transmission mode probes the local structure around V$^{4+}$ as well as any V$^{3+}$ resulted from the ball milling-induced reduction, increase in the V$^{3+}$ content with ball milling time gives rise to increased distribution of the short vanadyl bond as shown in Figure S2. Thus, observed changes in the pre-edge region are consistent with variation in the vanadyl bond length and its distribution, confirming increased V$^{3+}$ content with ball milling time.

**The $^7$Li and $^{31}$P Fermi contact shifts:**

Fermi contact shifts of the pristine LVPO structure and structure-B were calculated with single point energy calculations using BS-II. All calculations (single point and geometry optimizations)
for both structures were performed in the ferromagnetic state with a total energy converge criteria of $2.72 \times 10^{-6}$ eV, a Monkhorst-Pack mesh of $8 \times 8 \times 8$ and integral tolerances of $10^{-7}$, $10^{-7}$, $10^{-7}$, $10^{-7}$ and $10^{-14}$ as defined in the CRYSTAL14 documentation. In order to scale the Fermi contact shifts calculated from DFT at 0 K in the ferromagnetic state into the paramagnetic regime, the approach previously reported was adopted,\(^4\) in which the DFT calculated hyperfine coupling constant $A_{iso}$, is multiplied by a magnetic scaling factor, $\Phi$, defined as:

$$\Phi = \frac{B_0 \mu_{eff}^2}{3 k_B g_e \mu_B S_{form} (T-\theta)} $$

where $B_0$ is the external magnetic field, $k_B$ is Boltzmann’s constant, $S_{form}$ is the formal spin angular momentum quantum number of V\(^{4+}\) (equal to 1/2), $g_e$ is the free electron $g$ factor (equal to 2.0023), $\mu_B$ is the Bohr magneton, $T$ is the experimental temperature, $\mu_{eff}$ is the effective magnetic moment and $\theta$ is the Weiss constant. The value of $T$ at 60 kHz MAS was taken as 340 K to account for frictional heating. The values of $\mu_{eff}$ and $\theta$ were approximated 1.732 $\mu_B$ (spin only) and 0 K (Curie spin), respectively, as LiVOPO\(_4\) has previously been shown to adopt weak Curie-Weiss type paramagnetism.\(^5\) The scaling factor at 340 K was calculated as, $\Phi = 9.285 \times 10^{-3}$.

**Table S2.** Computed \(^7\)Li and \(^{31}\)P Fermi contact shifts for Li and P sites in model LVPO structure (structure-B).

| Hybrid Functional | \(^7\)Li Fermi Contact Shift (ppm) | \(^{31}\)P Fermi Contact Shift (ppm) |
|------------------|----------------------------------|----------------------------------|
|                  | Lia                              | Lib                              | Pa | Pb   |
| HYB20            | 22                               | 55                               | 2194 | 1608 |
| HYB35            | 18                               | 37                               | 1604 | 1238 |

\(^7\)Li NMR fitting procedure: The \(^7\)Li NMR spectra of the HEBM samples shown in Figure 6(b) were deconvoluted using the DMFIT software.\(^6\) For the 0.5 h HEBM sample, the two distinct Li
environments at 79 ppm (peak 1) and 4 ppm (peak 2) were fit with narrow Lorentzian peaks. A broad Gaussian peak (peak 3) at 43 ppm was also required to adequately fit the spectrum, suggesting the presence of a distribution of Li environments as a result of disorder. The 1\textsuperscript{st} and 2\textsuperscript{nd} order sidebands associated with each peak were also included in the fit. In the final step of the fitting procedure, the peak position, width and intensity of all of the isotropic peaks was allowed to vary, in addition to the peak intensity of the 1\textsuperscript{st} and 2\textsuperscript{nd} order sidebands.

The deconvolution of the 0.5 h HEBM samples was subsequently used as the starting point for the fit of the other spectra at different HEBM times (0.2, 0.3, 0.4, 0.6 and 0.7 h) in Figure 6(b). For each spectrum, a multistep procedure was used in which initially only the peak amplitudes were allowed to vary, with the peak positions and peak widths fixed to the values found for the 0.5 h sample. In the second step only the peak amplitudes and the peak positions were allowed to vary and in the final step, all parameters (peak amplitude, position and width) were allowed to vary. The resulting peak positions and widths are shown in Figure S4. By using the multistep fitting procedure, large, unphysical variations in the peak widths and peak positions were minimized.

![Figure S4](image.png)

**Figure S4.** Variation in the (a) $^7$Li NMR shift and (b) peak width of the three Li environments in ball milled LVPO as a function of HEBM time.
\textbf{\textsuperscript{31}P NMR fitting procedure:}

The \textsuperscript{31}P NMR spectrum of the 0.5 h HEBM sample was deconvoluted using a similar approach to the \textsuperscript{7}Li NMR spectra. The P1 and P2 environments that were present in the pristine LVPO material (Figure 7(a)) were fit with two Gaussian peaks at 1600 ppm (peak 1) and 1519 (peak 2), respectively, with widths of 123 and 382 ppm, respectively. A very broad (2514 ppm) Gaussian type peak was also included at 1889 ppm (peak 3). 1\textsuperscript{st} and 2\textsuperscript{nd} order sidebands were included in the fit for peak 1 and peak 2, but were omitted for peak 3. In the final step of the fitting procedure, the peak positions, widths and amplitudes of all of the isotropic peaks were allowed to vary, in addition to the amplitudes of the spinning sidebands. A direct comparison of the integrated intensities of the peaks was not attempted due to the very fast relaxation of peak 3, which meant that the majority of the signal was lost during the echo pulse sequence, even at 60 kHz MAS.

\textbf{DFT optimized LVPO structures:}

The structure of pristine LVPO with \textit{P\bar{T}} symmetry from previous reported\textsuperscript{7} was fully optimized (atomic positions and unit cell parameters) with BS-I. A quasi-Newtonian algorithm was used for the optimization with RMS convergence criteria of $8.16 \times 10^{-3}$ and $3.27 \times 10^{-2}$ eV, for forces and displacements respectively. To investigate the effect of Li ordering on the structure, a second structure was created, in which the Li ordering along the [110] direction of the cell was altered. This structure was created by removing two of the Li sites from the lowest energy structure of \textit{\varepsilon}-Li\textsubscript{1.5}VOPO\textsubscript{4} found in previous publication.\textsuperscript{7} This structure, which will subsequently be referred to as structure-B, was fully optimized with BS-I using the same convergence criteria as the pristine LVPO cell.
Table S3. Values of optimized unit cell parameters for the pristine and metastable (structure-B) structures of LVPO calculated with the HYB20 (20 % Hartree Fock exchange) and HYB35 (35 % Hartree Fock exchange) hybrid functionals.

| Structure              | Lattice Parameters | Angles |
|------------------------|--------------------|--------|
|                        | a (Å)   | b (Å)   | c (Å) | α (°) | β(°) | γ(°) |
| Experimental           | 6.746   | 7.207   | 7.928 | 89.82 | 91.28 | 116.91 |
| Pristine LVPO (HYB20)  | 6.792   | 7.147   | 7.832 | 89.78 | 91.85 | 116.82 |
| Pristine LVPO (HYB35)  | 6.771   | 7.109   | 7.802 | 89.83 | 91.81 | 116.86 |
| LVPO Structure-B (HYB20)| 6.741  | 7.059   | 7.999 | 89.89 | 89.68 | 115.41 |
| LVPO Structure-B (HYB35)| 6.718  | 7.021   | 7.972 | 89.90 | 89.82 | 115.37 |
Table S4. Atomic coordinates for DFT optimized pristine LVPO structures using the HYB20 (20 \% Hartree Fock exchange) and HYB35 (35 \% Hartree Fock exchange) hybrid functionals.

| Atom  | HYB20  | HYB35  |
|-------|--------|--------|
|       | x      | y      | z      | x      | y      | z      |
| Li (Li2) | 0.7896 | 0.7022 | 0.9284 | 0.7900 | 0.7038 | 0.9284 |
| Li (Li1) | 0.3080 | 0.8250 | 0.4283 | 0.3078 | 0.8239 | 0.4284 |
| Li (Li1) | 0.6921 | 0.1750 | 0.5717 | 0.6923 | 0.1762 | 0.5716 |
| Li (Li2) | 0.2604 | 0.2978 | 0.0716 | 0.2101 | 0.2962 | 0.0716 |
| V      | 0.2442 | 0.5267 | 0.7353 | 0.2442 | 0.5269 | 0.7355 |
| V      | 0.7505 | 0.9691 | 0.2330 | 0.7504 | 0.9690 | 0.2332 |
| V      | 0.2496 | 0.0309 | 0.7671 | 0.2496 | 0.0310 | 0.7668 |
| V      | 0.7558 | 0.4733 | 0.2647 | 0.7558 | 0.4731 | 0.2645 |
| P (P2) | 0.7327 | 0.7597 | 0.5908 | 0.7328 | 0.7596 | 0.5911 |
| P (P2) | 0.2673 | 0.2403 | 0.4093 | 0.2672 | 0.2404 | 0.4090 |
| P (P1) | 0.7702 | 0.2474 | 0.9081 | 0.7702 | 0.2474 | 0.9079 |
| P (P1) | 0.2298 | 0.7526 | 0.0920 | 0.2298 | 0.7526 | 0.0922 |
| O      | 0.4453 | 0.9195 | 0.1774 | 0.4451 | 0.9186 | 0.1777 |
| O      | 0.9436 | 0.9197 | 0.6839 | 0.9435 | 0.9189 | 0.6842 |
| O      | 0.7244 | 0.7423 | 0.1615 | 0.7248 | 0.7426 | 0.1619 |
| O      | 0.2623 | 0.5829 | 0.9908 | 0.2616 | 0.5830 | 0.9907 |
| O      | 0.9200 | 0.3449 | 0.7540 | 0.9205 | 0.3452 | 0.7547 |
| O      | 0.5731 | 0.6482 | 0.7369 | 0.5729 | 0.6483 | 0.7365 |
| O      | 0.2756 | 0.2577 | 0.8385 | 0.2752 | 0.2574 | 0.8381 |
| O      | 0.3629 | 0.1201 | 0.5272 | 0.3613 | 0.1198 | 0.5269 |
| O      | 0.4269 | 0.3518 | 0.2631 | 0.4271 | 0.3517 | 0.2635 |
| O      | 0.7377 | 0.4171 | 0.0093 | 0.7384 | 0.4170 | 0.0094 |
| O      | 0.0564 | 0.0803 | 0.3161 | 0.0565 | 0.0811 | 0.3158 |
| O      | 0.8758 | 0.1420 | 0.0293 | 0.8741 | 0.1412 | 0.0289 |
| O      | 0.1243 | 0.8580 | 0.9707 | 0.1259 | 0.8588 | 0.9711 |
| O      | 0.2247 | 0.3987 | 0.5132 | 0.2255 | 0.3991 | 0.5130 |
| O      | 0.0800 | 0.6551 | 0.2460 | 0.0795 | 0.6548 | 0.2453 |
| O      | 0.7697 | 0.2606 | 0.3320 | 0.7693 | 0.2608 | 0.3319 |
| O      | 0.5547 | 0.8085 | 0.8226 | 0.5549 | 0.8014 | 0.8223 |
| O      | 0.2303 | 0.7394 | 0.6680 | 0.2307 | 0.7392 | 0.6681 |
| O      | 0.7753 | 0.6013 | 0.4868 | 0.7745 | 0.6009 | 0.4870 |
| O      | 0.6371 | 0.8799 | 0.4728 | 0.6387 | 0.8802 | 0.4731 |
Table S5. Atomic coordinates for DFT optimized metastable LVPO structure (structure-B) using the HYB20 (20 % Hartree Fock exchange) and HYB35 (35 % Hartree Fock exchange) hybrid functionals.

| Atom  | HYB20     |          |          | HYB35     |          |          |
|-------|-----------|----------|----------|-----------|----------|----------|
|       | x         | y        | z        | x         | y        | z        |
| Li (Lib) | 0.6410 | 0.6380 | 0.9266 | 0.6379 | 0.6368 | 0.9283 |
| Li (Lib) | 0.1408 | 0.6373 | 0.4267 | 0.1380 | 0.6367 | 0.4283 |
| Li (Lia) | 0.1166 | 0.1232 | 0.0543 | 0.1209 | 0.1265 | 0.0562 |
| Li (Lia) | 0.6156 | 0.1225 | 0.5840 | 0.6208 | 0.1265 | 0.5561 |
| V      | 0.7370 | 0.0146 | 0.2588 | 0.7372 | 0.0150 | 0.2589 |
| V      | 0.7394 | 0.5182 | 0.2337 | 0.7390 | 0.5174 | 0.2335 |
| V      | 0.2368 | 0.0146 | 0.7589 | 0.2372 | 0.0151 | 0.7589 |
| V      | 0.2394 | 0.5182 | 0.7337 | 0.2390 | 0.5174 | 0.7336 |
| P (Pa) | 0.7499 | 0.7364 | 0.5861 | 0.7484 | 0.7377 | 0.5858 |
| P (Pb) | 0.2408 | 0.2462 | 0.4084 | 0.2423 | 0.2448 | 0.4078 |
| P (Pa) | 0.2500 | 0.7365 | 0.0861 | 0.2484 | 0.7377 | 0.0858 |
| P (Pb) | 0.7408 | 0.2463 | 0.9084 | 0.7423 | 0.2448 | 0.9078 |
| O      | 0.9310 | 0.3957 | 0.7992 | 0.9290 | 0.3898 | 0.7950 |
| O      | 0.2526 | 0.7422 | 0.6586 | 0.2485 | 0.7400 | 0.6597 |
| O      | 0.3164 | 0.1122 | 0.5235 | 0.3204 | 0.1143 | 0.5245 |
| O      | 0.2305 | 0.2324 | 0.8284 | 0.2334 | 0.2332 | 0.8292 |
| O      | 0.9205 | 0.8583 | 0.7196 | 0.9221 | 0.8643 | 0.7150 |
| O      | 0.5529 | 0.5763 | 0.6886 | 0.5540 | 0.5798 | 0.6908 |
| O      | 0.8428 | 0.6231 | 0.4637 | 0.8380 | 0.6212 | 0.4644 |
| O      | 0.4206 | 0.8584 | 0.2196 | 0.4221 | 0.8642 | 0.2150 |
| O      | 0.1772 | 0.8836 | 0.9852 | 0.1726 | 0.8815 | 0.9838 |
| O      | 0.5598 | 0.1011 | 0.7877 | 0.5586 | 0.0969 | 0.7907 |
| O      | 0.4309 | 0.3956 | 0.2991 | 0.4290 | 0.3898 | 0.2949 |
| O      | 0.0598 | 0.1011 | 0.2877 | 0.0586 | 0.0969 | 0.2907 |
| O      | 0.8165 | 0.1122 | 0.0235 | 0.8204 | 0.1142 | 0.0245 |
| O      | 0.0529 | 0.5763 | 0.1886 | 0.0540 | 0.5798 | 0.1908 |
| O      | 0.1468 | 0.3728 | 0.5153 | 0.1522 | 0.3746 | 0.5139 |
| O      | 0.6772 | 0.8835 | 0.4852 | 0.6725 | 0.8815 | 0.4838 |
| O      | 0.3428 | 0.6231 | 0.9637 | 0.3380 | 0.6212 | 0.9644 |
| O      | 0.6467 | 0.3729 | 0.0153 | 0.6522 | 0.3746 | 0.0139 |
| O      | 0.7306 | 0.2324 | 0.3284 | 0.7334 | 0.2332 | 0.3292 |
| O      | 0.7525 | 0.7422 | 0.1586 | 0.7485 | 0.7400 | 0.1597 |
Table S6. Discharge capacities of ball-milled LVPO in high-voltage (HV, 4.5-2.5 V) and low-voltage (LV, 2.5-1.6 V) regimes.

| Discharge capacity in HV (mAh g⁻¹) | Discharge capacity in LV (mAh g⁻¹) |
|-----------------------------------|-----------------------------------|
| HEBM 0.2 h                        | 123                               | 141                           |
| HEBM 0.3 h                        | 124                               | 152                           |
| HEBM 0.4 h                        | 133                               | 151                           |
| HEBM 0.5 h                        | 152                               | 151                           |
| HEBM 0.6 h                        | 117                               | 140                           |
| HEBM 0.7 h                        | 116                               | 135                           |

Figure S5. Morphology of (a) super P carbon, (b) acetylene black, (c) graphene nanoplatelets, (d) graphite; LVPO ball-milled 0.5 hours with (e) acetylene black, (f) graphene nanoplatelets and (g) graphite.
Ionic conductivity ($\sigma_i$) and electronic conductivity ($\sigma_e$) of LVO:

The pellet of LVO powder was die-pressed and sintered, then coated with Ag conductor paste on both sides to form blocking electrodes. The size of pellet was 1.3 cm diam and 0.08-0.1 cm thick. EIS was performed at room temperature at a frequency range from 200 kHz to 1 mHz with applying amplitude of 5 mV. The impedance spectra are shown in Figure S6. The intercept of the depressed semi-circle with $Z_{Re}$ axis at high frequency is the total resistance $R_{total}$, corresponding to the electronic and ionic resistance in parallel connection ($R_i R_e / R_i+R_e$). The depressed semi-circle at low frequency is caused by the interfacial resistance. The inclined straight line of Warburg response at low frequency is attributed to stoichiometric polarization in LVO. The electronic resistance $R_e$ was achieved by four-probes d.c. methods, performed on Keithley 2400 sourcemeter. The measured $\sigma_i$ and $\sigma_e$ of LVO is $3.6 \times 10^{-7}$ and $1.3 \times 10^{-8}$ S cm$^{-1}$, respectively.

Figure S6. The conductive impedance spectra of LVO and the equivalent circuit model.
Figure S7. Charge-discharge curve of LVO at voltage range of 1.6–4.5 V by the rate of C/5.

Figure S8. (a) rate capability and capacity retention (inset), and (b) discharge capacities upon extended cycling at C/5 (0.076 mA cm$^{-2}$) of uncoated LVPO and LVPO/LVO plotted per g of LVPO+LVO.

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