Deconvolving lithium-ion redox in vanadium-iron oxide aerogels using X-ray absorption spectroscopy and density functional theory

Ryan H. DeBlock,[1] Michelle D. Johannes,[2] Hunter O. Ford,[1] Michael W. Swift,[2] Debra R. Rolison,[1] and Jeffrey W. Long[1]

[1] *Code 6170, Surface Chemistry Branch, U.S. Naval Research Laboratory, Washington, DC, USA*

[2] *Code 6390, Center for Computational Science, U.S. Naval Research Laboratory, Washington, DC 20375, USA*

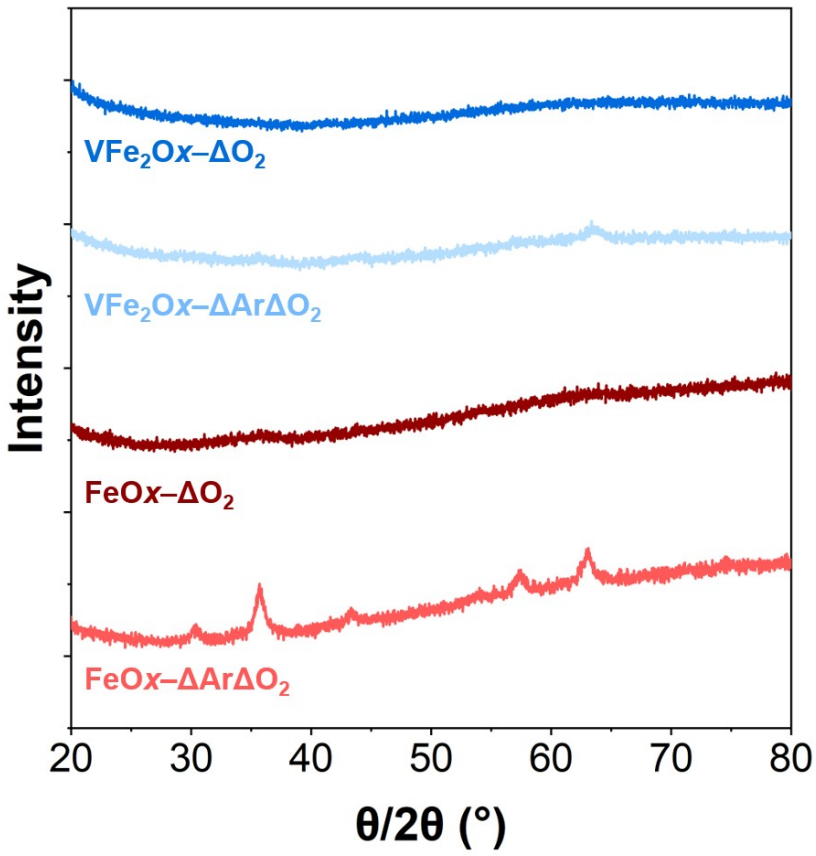

Fig. S1 X-ray diffractograms of $VFe_2Ox–\Delta O_2$, $VFe_2Ox–\Delta Ar\Delta O_2$, $FeOx–\Delta O_2$, and $FeOx–\Delta Ar\Delta O_2$ aerogels from top to bottom.

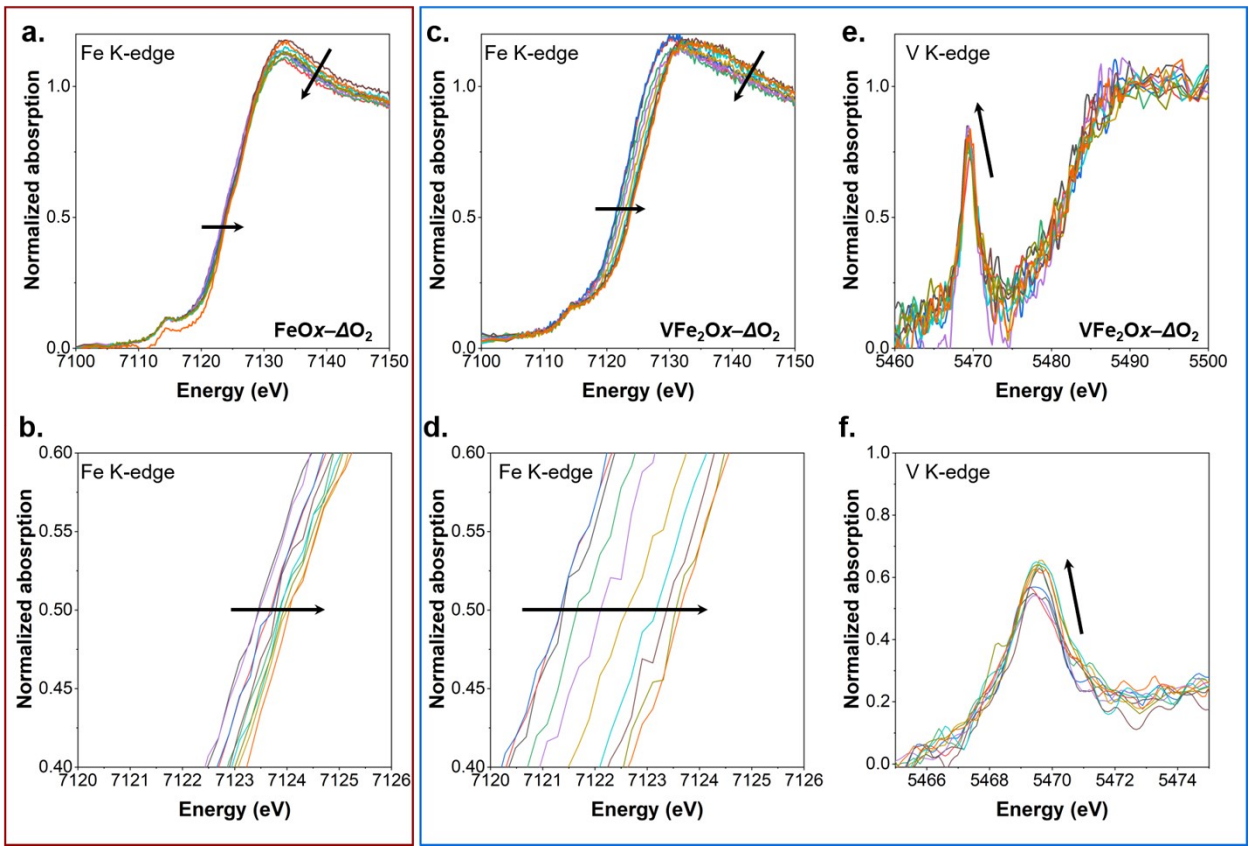

Fig. S2 in situ XANES spectra of pouch cells at the Fe K-edge for **a., b.** FeOx–ΔO_2 and **c., d.** VFe_2Ox–ΔO_2 aerogels upon delithiation (charge). **e., f.** In situ XANES spectra at the V K-edge for VFe_2Ox–ΔO_2 upon delithiation (charge). Panels b., d., and f. are inset views of panels a., c., and e., respectively. Arrows denote the direction of delithiation with respect to voltage.

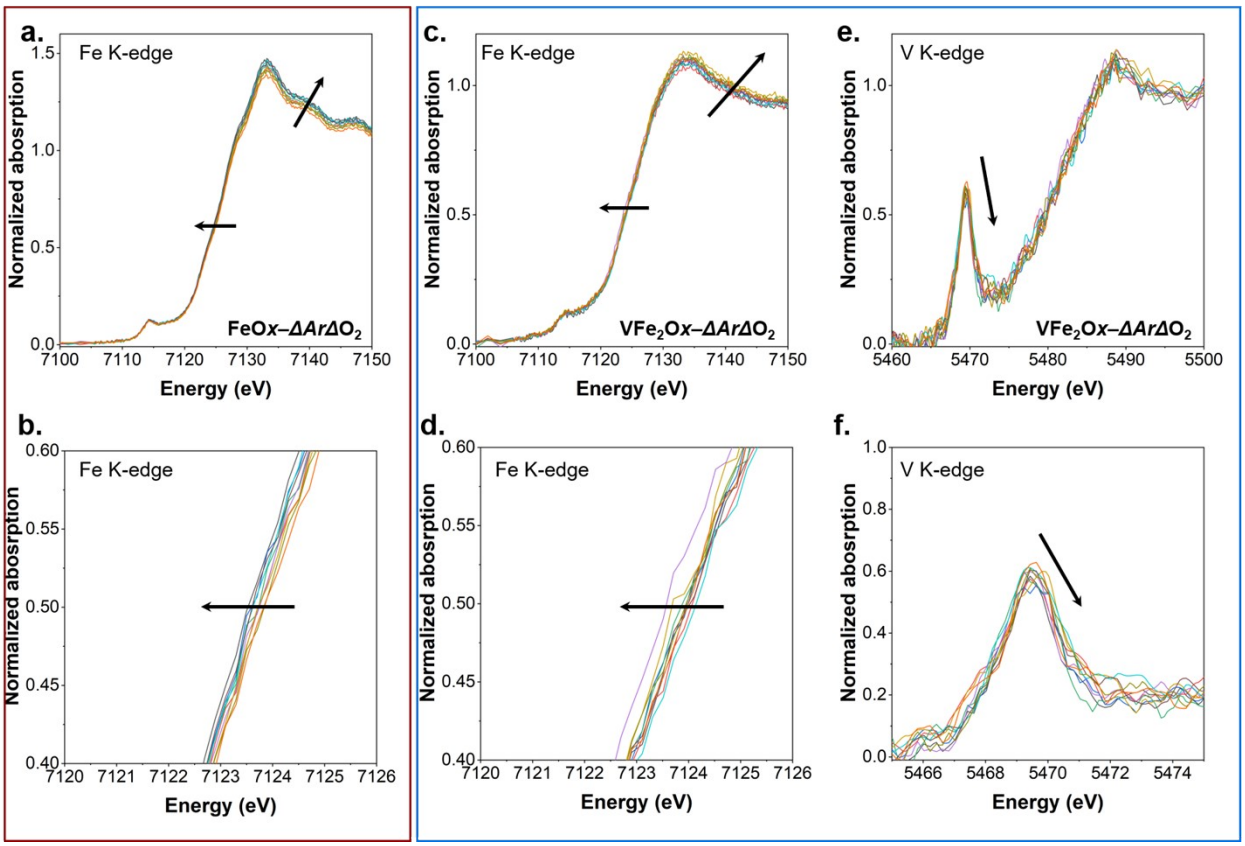

Fig. S3 in situ XANES spectra of pouch cells at the Fe K-edge for **a., b.** FeOx–ΔArΔO_2 and **c., d.** $VFe_2O$$x$–ΔArΔ$O_2$ aerogels upon lithiation (discharge). **e., f.** In situ XANES spectra at the V K-edge for $VFe_2O$$x$–ΔArΔ$O_2$ upon lithiation (discharge). Panels b., d., and f. are inset views of panels a., c., and e., respectively. Arrows denote the direction of lithiation with respect to voltage.

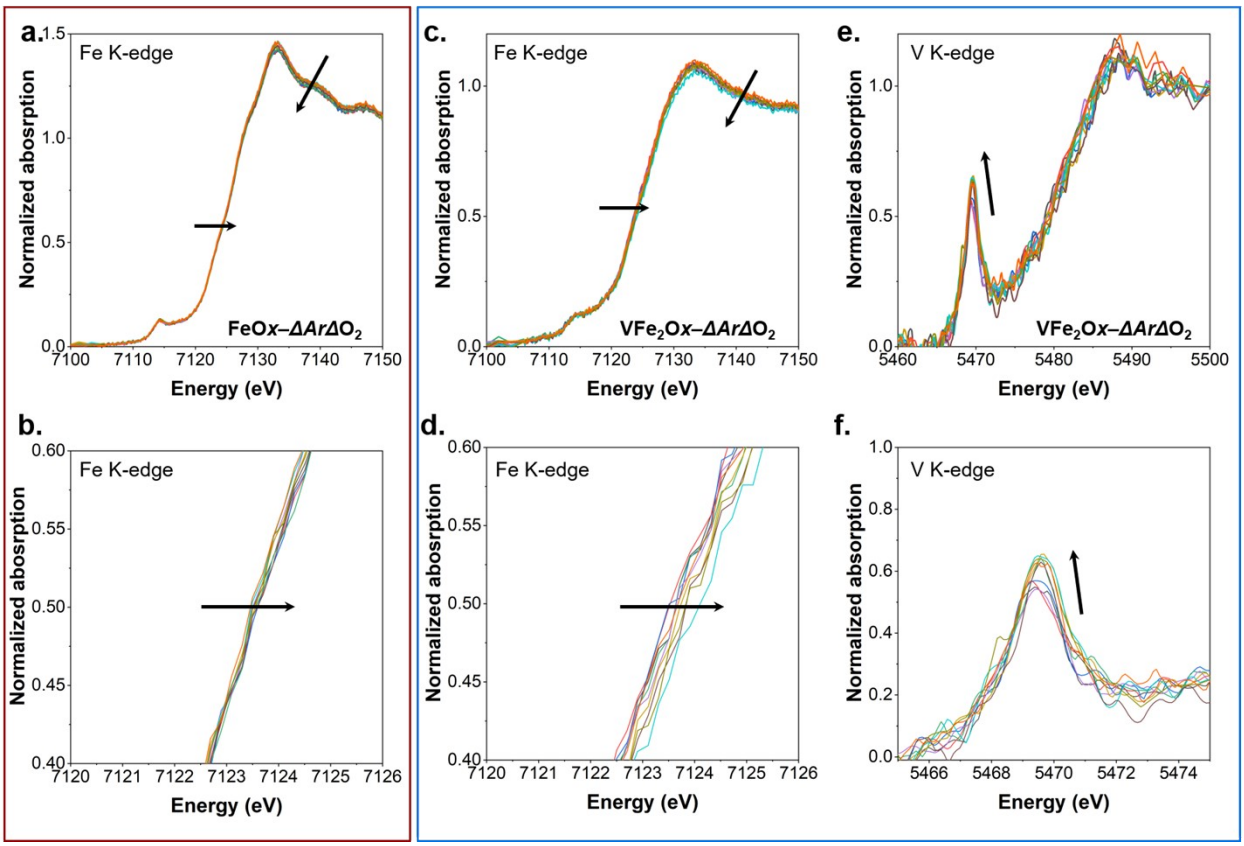

Fig. S4 in situ XANES spectra of pouch cells at the Fe K-edge for **a., b.** FeOx–ΔArΔO_2 and **c., d.** $VFe_2O$$x$–ΔArΔ$O_2$ aerogels upon delithiation (charge). **e., f.** In situ XANES spectra at the V K-edge for $VFe_2O$$x$–ΔArΔ$O_2$ upon delithiation (charge). Panels b., d., and f. are inset views of panels a., c., and e., respectively. Arrows denote the direction of delithiation with respect to voltage.

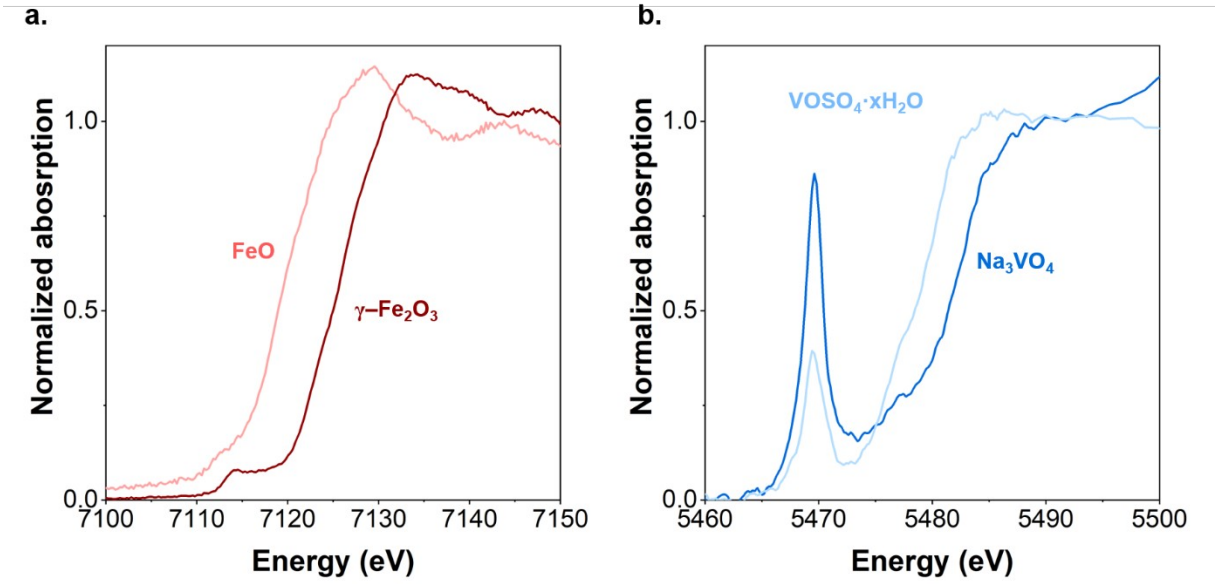

Fig. S5 XANES spectra of **a.** Fe standards FeO (Fe^{2+}) and γ-Fe_2O_3 (Fe^{3+}) and **b.** V standards $VOSO_4 \cdot H_2O$ (V^{4+}) and Na_3VO_4 (V^{5+}).

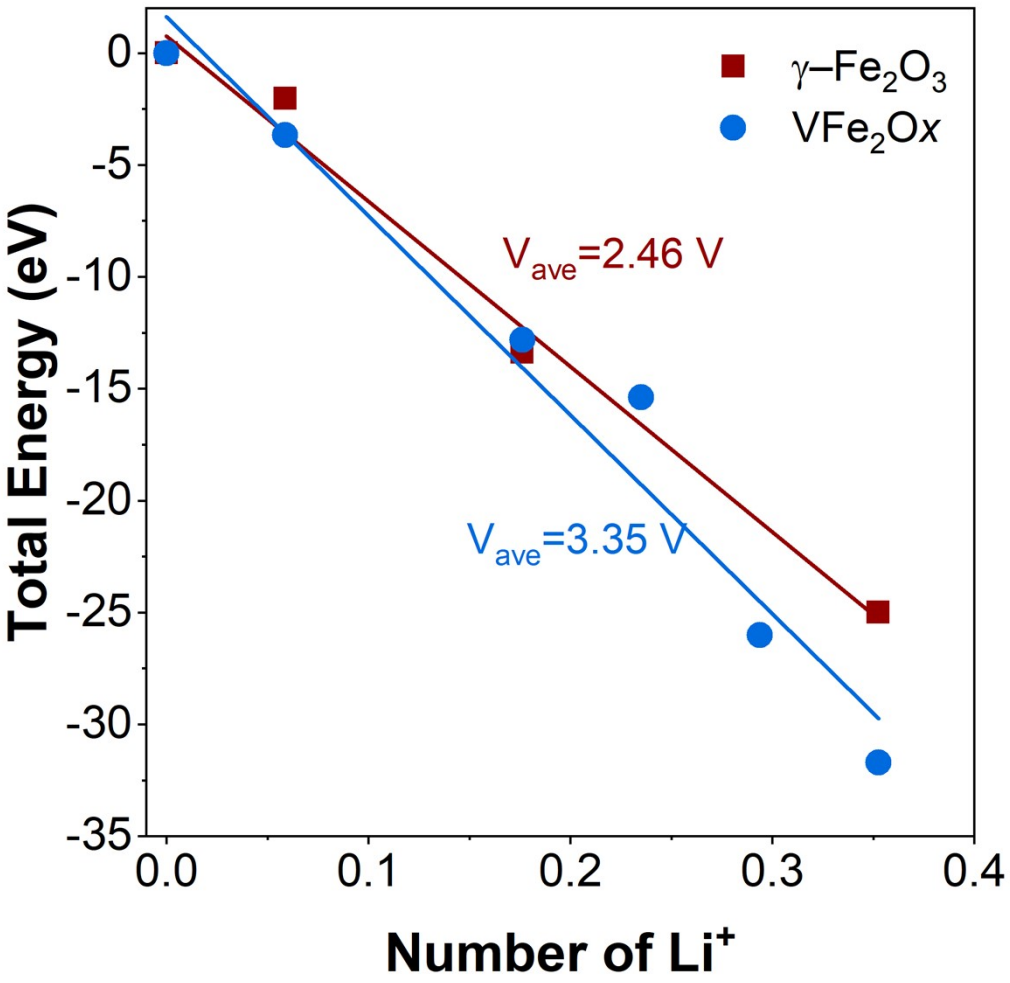

Fig. S6 Total energy for γ-Fe_2O_3 and VFe_2Ox calculated by DOS as a function of inserted Li^+. Straight lines are fit to these data to calculate an average potential of insertion for each material.

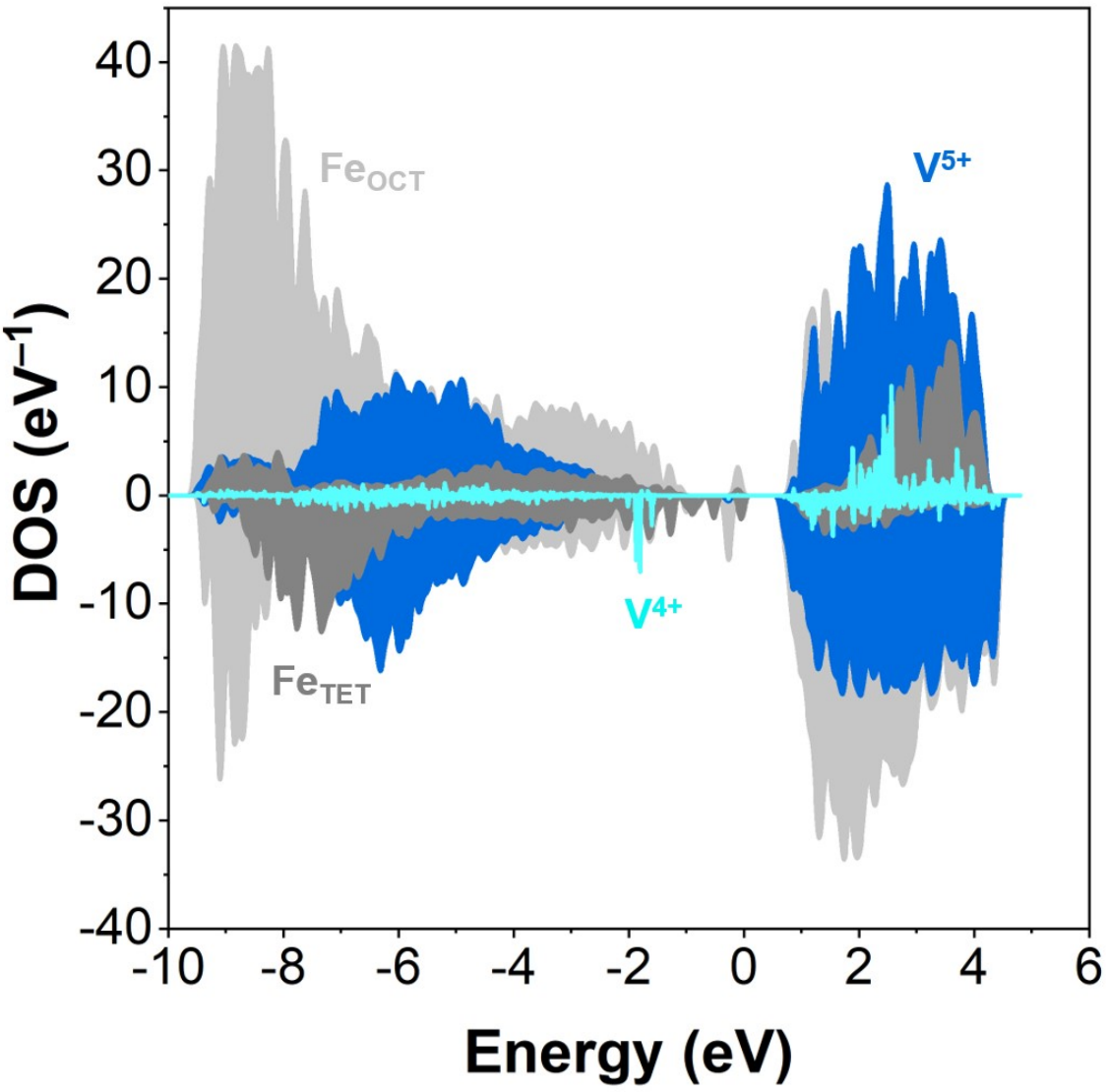

Fig. S7 pDOS of VFe_2Ox for the case where two oxygen vacancies where located next to a V atom leading to under-coordinated V^{4+}.

Derivation of hybridization strength from first-order perturbation theory

Assuming a two-state system with energies separated by U and isolated from one another (no interaction between states), the simple Hamiltonian matrix with eigenvalues, λ, looks like:

$$\begin{bmatrix} 0-\lambda & 0 \\ 0 & U-\lambda \end{bmatrix}$$

which, when diagonalized, produces eigenvalues:

$\lambda = 0, U$

If these states are then allowed to hybridize with a strength of *t*, defined formally as the matrix element between the two states $t \equiv \langle 1|H|2\rangle$, then the Hamiltonian matrix becomes

$$\begin{bmatrix} 0-\lambda & t \\ t & U-\lambda \end{bmatrix}$$

which can be diagonalized to yield eigenvalues of

$$\lambda = \frac{U \pm \sqrt{U^2 + 4\frac{t^2}{U^2}}}{2}$$

which can be trivially rewritten as:

$$\lambda = \frac{U \pm U\sqrt{1 + 4\frac{t^2}{U^2}}}{2}$$

Assuming that $t^2 << U^2$, a Taylor expansion can be applied to the radical and eigenvalues become:

$\lambda = \frac{U}{2} \pm \frac{U}{2}(1+4t^2/U^2 + \ldots)$ where higher order terms in the expansion are neglected

This can be simplified to:

$$\lambda = 0 - \frac{2t^2}{U}, \quad U + \frac{2t^2}{U}$$

indicating that the lower energy state is lowered further by $\frac{2t^2}{U}$ and the upper state further raised by $\frac{2t^2}{U}$. Eigenstates, naturally, experience mixing at the same order, namely ~ t^2/U.

Table S1 Brunauer–Emmett–Teller (BET) surface areas and Barrett–Joyner–Halenda (BJH) pore volumes VFe_2Ox and FeOx aerogels

Sample	BET Surface Area ($m^2\ g^{-1}$)	BJH pore volume ($cm^3\ g^{-1}$)	Reference
VFe_2Ox–ΔO_2	231	1.3	a.
VFe_2Ox–$\Delta Ar\Delta O_2$	156	0.87	a.
$FeOx$–ΔO_2	416	2.3	a.
$FeOx$–$\Delta Ar\Delta O_2$	148	1.01	This work

a. C. N. Chervin, J. S. Ko, B. W. Miller, L. Dudek, A. N. Mansour, M. D. Donakowski, T. Brintlinger, P. Gogotsi, S. Chattopadhyay, T. Shibata, J. F. Parker, B. P. Hahn, D. R. Rolison and J. W. Long, *J. Mater. Chem. A*, 2015, **3**, 12059-12068.

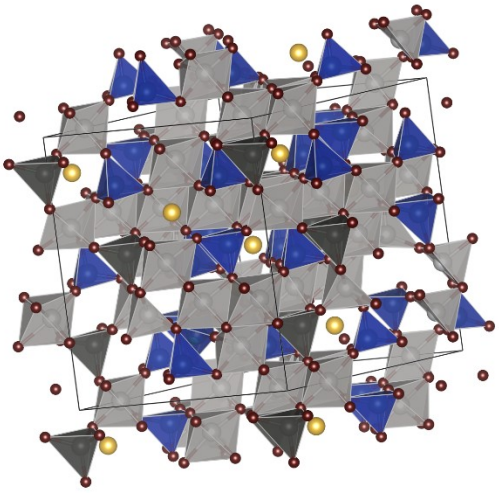

Fig. S8 Structure schematic of highly lithiated VFe_2Ox. $Fe_{oct}O_6$ octahedra are shown in light grey, $Fe_{tet}O_4$ tetrahedra are show in dark grey, and tetrahedral V sites are in blue. Li atoms were originally placed randomly in areas where they were able to fit without unreasonably small distances between them and other atoms. After the system (lattice and ions) is relaxed, the shown structure was achieved.