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Defective by design: Vanadium-substituted iron oxide nanoarchitectures as cation-insertion hosts for electrochemical charge storage

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Vanadium-substituted iron oxide aerogels (2:1 Fe:V ratio; VFe\textsubscript{2}O\textsubscript{x}) are synthesized using an epoxide-initiated sol–gel method to form high surface-area, mesoporous materials in which the degree of crystallinity and concentration of defects are tuned via thermal treatments under controlled atmospheres. Thermal processing of the X-ray amorphous, as-synthesized VFe\textsubscript{2}O\textsubscript{x} aerogels at 300°C under O\textsubscript{2}-rich conditions removes residual organic byproducts while maintaining a highly defective γ-Fe\textsubscript{2}O\textsubscript{3}–like local structure with minimal long-range order and vanadium in the +5 state. When as-synthesized VFe\textsubscript{2}O\textsubscript{x} aerogels are heated under low partial pressure of O\textsubscript{2} (e.g., flowing argon), a fraction of vanadium sites are reduced to the +4 state, driving crystallization to a Fe\textsubscript{3}O\textsubscript{4}–like cubic phase. Subsequent thermal oxidation of this nanocrystalline VFe\textsubscript{2}O\textsubscript{x} aerogel re-oxidizes vanadium +4 to +5, creating additional cation vacancies and re-introducing disordered oxide domains. We correlate the electrochemical charge-storage properties of this series of VFe\textsubscript{2}O\textsubscript{x} aerogels with their degree of order and chemical state, as verified by X-ray diffraction, X-ray photoelectron spectroscopy, and X-ray absorption spectroscopy. We find that the disordered O\textsubscript{2}-heated VFe\textsubscript{2}O\textsubscript{x} aerogel yields the highest Li\textsuperscript{+}- and Na\textsuperscript{+}-insertion capacities among this series, approaching 130 mA h g\textsuperscript{-1} and 70 mA h g\textsuperscript{-1}, respectively. Direct heat-treatment of the VFe\textsubscript{2}O\textsubscript{x} aerogel in flowing argon to yield the partially reduced, nanocrystalline form results in significantly lower Li\textsuperscript{+}-insertion capacity (77 mA h g\textsuperscript{-1}), which improves to 105 mA h g\textsuperscript{-1} by thermal oxidation to create additional vacancies and structural disorder.
Introduction

High-performance materials used as positive electrodes for rechargeable Li-ion batteries often contain expensive, toxic, and/or strategic metals (in the form of pure or mixed-metal oxides such as LiCoO$_2$), driving the search for less expensive, nontoxic alternatives. One such example is LiFePO$_4$, which offers a thermodynamically favorable Li$^{+}$-insertion potential of ~3.5 V vs. Li and a high reversible capacity (160 mA h g$^{-1}$), in conjunction with the cost and environmental benefits inherent to iron-based materials. Certain iron oxides (FeO$_x$), particularly those that have cation-defective structures, also exhibit promise as positive electrode materials. For example, maghemite (γ-Fe$_2$O$_3$, more accurately denoted as Fe$^{3+}_{2.67}$$\square_{0.33}$O$_4$) is a cation-deficient spinel phase that inserts Li$^+$ into structural cation vacancies at more positive potentials than observed in the defect-free analogue, magnetite (Fe$_3$O$_4$). The cation-vacancy population of the γ-Fe$_2$O$_3$ structure can be further increased by substituting a fraction of the Fe$^{3+}$ sites with metal cations of higher oxidation state, such as Mo$^{6+}$ or V$^{5+}$. We recently reported that a nanocrystalline Mo-substituted ferrite (Mo$_{0.59}$Fe$_{1.50}$$\square_{0.91}$O$_4$$\cdot$nH$_2$O) provides >4× improvement in specific capacity for Li$^+$-insertion relative to an analogous γ-Fe$_2$O$_3$ material. The population of electrochemically active defects in metal oxides can also be amplified when these materials are expressed in nanoscale forms, ranging from hollow nanospheres to three-dimensionally (3D) ultraporous nanoarchitectures such as aerogels. Aerogels exhibit high specific surface areas (100–600 m$^2$ g$^{-1}$) that encourage surface-sited defect formation, while providing other structural characteristics beneficial to electrochemical functionality: (i) through-connected, covalently bonded networks of nanometric particles that electrically wire the electrode architecture; (ii) through-connected networks of mesopores and/or macropores that enable efficient diffusion and transport of molecules and ions; and (iii) nanoscale domains that minimize the solid-state diffusion distance for ion insertion.

Previous investigations of V$_2$O$_5$ aerogels as Li$^+$-insertion hosts illustrate how the aerogel framework can enhance electrochemical performance. For example, while microcrystalline V$_2$O$_5$ only intercalates ~2 Li$^+$ per formula unit, V$_2$O$_5$ aerogels insert >4 Li$^+$ per formula unit (chemically or electrochemically). Spectroelectrochemical analysis of Li$^+$-insertion into V$_2$O$_5$ aerogels implies that beyond 2 Li$^+$ per V$_2$O$_5$, the increase in Li$^+$ content may not occur by traditional insertion mechanisms but rather by processes at accessible defect sites that are not accompanied by a change in the oxidation state of vanadium.
Herein, we combine these two materials design strategies to produce deliberately defective cation-insertion hosts based on V-substitution into a $\gamma$-Fe$_2$O$_3$–like structure that is expressed as an ultraporous, high surface-area aerogel. Vanadium-substituted iron oxide (2:1 Fe:V ratio; VFe$_2$O$_x$) aerogels are achieved using an epoxide-driven sol–gel synthesis$^{21,22,23,24}$ that yields amorphous oxides of the desired stoichiometry, but whose crystallinity and defective nature can be tuned by subsequent thermal processing under controlled atmospheres. We explore the cation-insertion properties of VFe$_2$O$_x$ aerogels as a function of crystalline order, V and Fe oxidation state, and surface area/porosity. Direct thermal processing under flowing O$_2$ at 300°C produces X-ray-amorphous VFe$_2$O$_x$ aerogels that exhibit reversible Li$^+$- and Na$^+$-insertion specific capacities approaching 130 mAh g$^{-1}$ and 70 mAh g$^{-1}$, respectively, a result of high specific surface area (231 m$^2$ g$^{-1}$), a defective $\gamma$-Fe$_2$O$_3$ local structure, and V present in the +5 oxidation state. The local and long-range atomic structures and the chemical state of the VFe$_2$O$_x$ aerogels as a function of thermal treatment were elucidated by X-ray absorption spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy; material morphology and composition were examined by electron microscopy and energy-dispersive spectroscopy.

**Experimental**

**VFe$_2$O$_x$ aerogel synthesis and processing**

The VFe$_2$O$_x$ aerogels were synthesized by adapting the alkoxide-precursor, epoxide-initiated sol–gel method$^{25}$ using an Fe-to-V ratio of 2:1. The use of vanadium salts rather than an alkoxide precursor led to precipitates rather than gels. In a typical synthesis, FeCl$_3$•6H$_2$O (3.0846 g; 97%, Sigma-Aldrich) was dissolved in 10 mL of ethanol (200 proof, Warner-Graham Company) via sonication and then chilled in an aqueous ice bath. In a second container, vanadium triisopropoxide (1.3832 g; 96%, Alfa Aesar; stored in a refrigerator at 35°C before use) was added drop-wise into 20 mL of ethanol pre-chilled in an aqueous ice bath. The vanadium solution was equilibrated for a few minutes and then chilled to ~78°C in a dry ice–ethanol bath. The two chilled solutions were combined with an additional 10 mL rinse with ethanol to ensure quantitative transfer of the Fe$^{3+}$; the V-Fe solution was equilibrated for ~3 min in the dry ice–ethanol bath. Next, 12 mL of propylene oxide (Sigma-Aldrich 99%; passed through a column of activated alumina and stored in a refrigerator at 35°C before use) was quickly added to the container and the solution was covered with Parafilm™. The solution was equilibrated for
~5 min in the –78°C bath and then placed in an aqueous ice bath and stirred for ~45 min, during which time the solution changed from translucent orange to dark reddish-brown. The sol was removed to ambient temperature and gelation occurred within 10 min. The gel was aged overnight with the Parafilm™ seal maintained; the mother liquor within the gel pores was then exchanged with several 200-mL aliquots of ethanol over a 24-h period to remove reaction byproducts, followed by several days of solvent exchange with 200-mL aliquots of acetone (certified ACS; Fisher Scientific).

The acetone-exchanged gels were transferred under excess acetone into a supercritical drier (Polaron, Quorum Technologies), and solvent-exchanged with liquid CO$_2$ at 10°C. The CO$_2$ was then taken to 44°C and 9 MPa, well beyond its supercritical point of 31°C and 7.4 MPa, before the pressure was released. For comparison, unsubstituted FeO$_x$ aerogels were prepared by the epoxide method using the FeCl$_3$•6H$_2$O precursor, ethanol solvent, and propylene oxide gel-initiator as described above (i.e., the same molar ratio of cations to epoxide and cation to solvent), but carried out under ambient temperature (~20°C).

The as-synthesized VFe$_2$O$_x$ and FeO$_x$ aerogels were calcined to 300°C in alumina boats within a calibrated tube furnace (MTI Corporation OTF-1200X) under flowing Ar or O$_2$ at ~50 cm$^3$ min$^{-1}$ with heating and cooling ramp rates of 1°C min$^{-1}$ and 4-h dwell times at the calcining temperature. Samples heated under high and low partial pressure of oxygen ($p_{O_2}$) are referred to as 300-O$_2$ and 300-Ar, respectively. The samples designated as 300-Ar-O$_2$ were first subjected to a low $p_{O_2}$ heat treatment, cooled to room temperature and then heated under high $p_{O_2}$ using the same temperature, ramp rate, and dwell time.

**Materials characterization**

Surface areas and pore-size distributions of the VFe$_2$O$_x$ and FeO$_x$ aerogels were measured using nitrogen physisorption (Micromeritics ASAP 2020 porosimeter). All samples were degassed at 80°C for 12 h, backfilled with N$_2$ at room temperature, and then immediately placed on the instrument for characterization. Surface area was determined from the linear portion of the adsorption isotherm using the model of Brunauer–Emmet–Teller. Pore size distributions were calculated from the entire adsorption isotherm data using Micromeritics DFTPlus software (DFT model for a cylindrical geometry and Halsey curve thickness).

Aerogel morphology was imaged using scanning electron microscopy (SEM; Carl Zeiss Leo
Supra 55 microscope operating at 5 keV) and transmission electron microscopy (TEM; JEOL JEM 2200FS microscope operating at 200 kV). Elemental analysis was made with the SEM using energy dispersive spectroscopy (EDS; operating at 20 keV). For SEM measurements, the aerogel powders were mounted onto aluminum SEM stubs using double-sided carbon tape; for TEM measurements, the powders were ground in isopropanol and drop cast onto lacey carbon substrates.

The temperatures necessary for crystallization and volatilization of synthesis byproducts as a function of calcining atmosphere were characterized using simultaneous thermoanalytical and calorimetric measurements with a Netzsch STA 449 F1 Jupiter thermogravimetric analyzer (TGA/DSC). Approximately 10 mg of as-synthesized aerogel was placed in an alumina crucible and equilibrated under the desired atmosphere for ~1 h before heating. The samples were heated to 550°C at 10°C min⁻¹ in either Ar or O₂.

Powder X-ray diffraction (PXRD) profiles were collected on a Rigaku SmartLab X-ray diffractometer with a fixed CuKα radiation (λ = 1.5406 Å). Scans were recorded from 20 to 80°2θ, with a 0.02° step size and an integration time of 1 s per step. For materials where the PXRD indicated crystallinity, average crystallite sizes were calculated from the peak indexed to the (400) peak of the magnetite crystal structure; we chose the (400) reflection because it is intense and sufficiently isolated to avoid peak overlap from other reflections. Synchrotron PXRD data for 300-Ar and 300-Ar-O₂ VFe₂Oₓ aerogels were collected at beamline 11-BM at the Advanced Photon Source at Argonne National Laboratory (λ = 0.413851 Å). The data were refined with the General Structure Analysis System (GSAS) with EXPGUI;²⁶,²⁷ models of maghemite (P₄₃2₁₂ ICDS #87121) and magnetite (Fd-3m, ICDS #20596) and assuming the stoichiometry for the aerogel was Fe₈ₓ/(8+x)V(24−8x)/(8+x)☐₃☐/(8+x)O₄ (x ≈ 2).

X-Ray Photoelectron Spectroscopy (XPS) was used to examine the chemical state and relative concentrations of Fe, V, and O using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer at a chamber pressure <5.0×10⁻⁸ torr and equipped with a monochromatic Al Kα source (1486.68 eV) using a 400-µm elliptical spot size. The VFe₂Oₓ aerogel specimens were packed into wells of the powder module sample holder. The spectra were obtained at an energy step-size of 0.15 eV by averaging 25 scans of the Fe 2p, V 2p, O 1s, C 1s, and Cl 2p regions (the Cl region was examined to ensure >99% conversion/removal of chloride). The spectra were analyzed with Avantage® software version 5.35 using a Shirley-derived background subtraction.
model and peak-shifting relative to the adventitious C$1s$ peak of 284.6 eV. The V$2p_{3/2}$ peaks were fitted with a floating Gaussian–Lorentzian ratio.

Room-temperature V and Fe K-edge X-ray absorption spectra of VFe$_2$O$_x$ and FeO$_x$ aerogels for as-synthesized materials and following heat treatments were collected in transmission mode at beamline 10-ID-B at the Advanced Photon Source at Argonne National Laboratory. The samples were prepared by attaching the powders to scotch tape and then folding several layers of the powder-tape assembly together; a method that gives reasonable results for homogenized powders such as aerogel materials. The energy scale was calibrated with respect to the first inflection point energies of the Fe and V foil standards at 7112.0 and 5465.0 eV, respectively. The pre-edge background was determined from a linear fit to the energy range of −150 to −30 eV relative to the edge energy. The normalization step was determined from a cubic polynomial fit over the energy range 150 to ~800 eV relative to the edge energy. The half-height energy was used to define the wave number k=0. The background for the extended X-ray absorption fine structure (EXAFS) was determined using cubic spline procedures over the range 2–12 Å$^{-1}$ with the FT range set to 3–11 Å with $k^3$-weighted EXAFS spectra and a Hanning window of 1.0 Å$^{-1}$. The XAFS data analysis was carried out using the IFEFFIT suite of programs (Athena and Artemis).$^{28,29}$

**Electrode preparation**

Aluminum foil current collectors (Alfa Aesar; either 0.5-mm thick, 99.9% metals basis or 0.13-mm thick, 99.9995% metals basis) for three-electrode and coin-cell configurations were prepared by sanding one side of the foil with 120-grit sand paper and then alkaline-etching in 1 M NaOH at ambient temperature for 20 min, rinsing with deionized water, and acid-etching at 80°C in 1 M HCl. The etched foils were rinsed with deionized water and air-dried at 100°C overnight. The current collectors for three-electrode half-cell configurations were 0.5-mm thick and cut into 2 cm × 1 cm pieces, whereas the foils for coin-cells were 0.13-mm thick and cut into $\frac{1}{2}''$-diameter disks.

Active cathode material inks were prepared by making a slurry in N-methyl-2-pyrrolidone (NMP; 99.5% anhydrous, Sigma-Aldrich) of 85% active material, 8% Super P carbon black (source) and 7% polyvinylidene fluoride binder (PVdF; Kynar® HSV 900). Approximately 15–20 mg of active material powder was combined with carbon in a mortar and pestle and ground
for ~3 min to ensure that the powders were well-mixed to which a 5% PVdF solution in NMP was added and the wet mixture ground for 15 min. As necessary, NMP was added drop-wise to maintain a consistency of warm honey. The slurry was applied to the current collector with a spatula and then air dried for ~1 h followed by vacuum drying overnight at 120°C. After drying, the electrodes were sandwiched between two weigh papers and pressed at 5000 psi and then immediately weighed and pumped into an Ar atmosphere glove box. For the half-cell electrodes, the slurries were painted onto a 1 cm × 1 cm area of the aluminum current collector, whereas for the coin-cell disks, the entire ½” face was painted with the slurry. The mass of active material was calculated as 85% of the weight of the applied film, as determined by the mass difference of the aluminum substrate before and after applying, drying, and pressing the film.

**Electrochemical characterization**

Cyclic voltammetric measurements were made with a Solartron SI1286 Electrochemical Interface using a three-electrode configuration in an Ar atmosphere glove box. For Li⁺-insertion experiments an electrolyte of 1 M LiPF₆ in 1:1:1 ethylene carbonate:diethyl carbonate:dimethyl carbonate (BASF) was used and the reference and auxiliary electrodes were made from Li foils (250-μm thick). The Na⁺-insertion experiments were made with Na-foil auxiliary and reference electrodes in an electrolyte comprising 1 M NaClO₄ in propylene carbonate (99.7% anhydrous, Sigma-Aldrich), which was prepared in an Ar atmosphere glove box and dried with molecular sieves (3 Å, Sigma-Aldrich) before use. The cathodes were cycled between 2.0 and 4.0 V vs. Li/Li⁺ or 1.7 and 3.7 V vs. Na/Na⁺ from 0.5 to 50 mV s⁻¹. The specific capacity was determined by averaging the integrated anodic and cathodic currents and normalizing to the mass of active material on the film.

Coin-cell measurements were performed in CR 2032 coin cells (MTI corporation) that consisted of (working outward from anode side) a Teflon®-separated negative electrode can, a stainless-steel spring, two stainless-steel spacers with a 250-μm–diameter Li-foil disc attached to the second spacer, two 2400 Celgard separators, the cathode film deposited on aluminum-foil current collector as described above, and a positive electrode can. The cells were assembled in an Ar-filled glove box. The cathode and the Celgard separator were infiltrated with the LiPF₆ electrolyte at 20 mm(Hg) for 4 h in the glove box antechamber and excess electrolyte was applied to the Li anode during cell assembly. The coin-cell cycling was controlled with an Arbin
BT2000 cycler, in the range of 2 V to 4 V at 10 mA g\(^{-1}\) of active material, starting with an initial charge step.

**Results and Discussion**

**Synthesis of VFe\(_2\)O\(_x\) aerogels**

The VFe\(_2\)O\(_x\) aerogels were synthesized using sol–gel protocols in which a proton-scavenging epoxide (propylene oxide) drives hydrolysis and condensation of metal(aquo-hydroxy) complexes to form metal-oxide gel networks; subsequent supercritical \(\text{CO}_2\) extraction of the liquid-filled gels produces monolithic aerogels.\(^{21}\) Epoxide-based sol–gel chemistry is a versatile route to synthesize iron oxides\(^{21,22,23,24}\) as well as other transition metal and rare-earth oxides (e.g., Y\(_2\)O\(_3\)-stabilized ZrO\(_2\), La\(_{0.85}\)Sr\(_{0.15}\)MnO\(_3\), NiCo\(_2\)O\(_4\), La\(_{0.33}\)Si\(_6\)O\(_{26}\), and Gd\(_{0.1}\)Ce\(_{0.9}\)O\(_2\)).\(^{25,30,31,32,33,34}\) Hydrated metal chlorides are the most common precursors due to their high solubility in alcohols and water, and because chloride ions act on the protonated epoxide via nucleophilic attack to shift the equilibrium of the hydrolysis/condensation reactions. Iron(III) chlorides behave ideally for epoxide-based sol–gel methods,\(^{35}\) but vanadium(III) chloride precursors hydrolyze too rapidly, preferentially forming precipitates rather than stable gels. We adapted our prior strategy for bimetallic oxide gels in which one of the metals was introduced as an alkoxide,\(^{25}\) and used vanadium tri-isopropoxide (V(\(^i\)OPr)\(_3\)), a well-known precursor for synthesizing V\(_2\)O\(_5\) aerogels.\(^{36}\) While more stable than vanadium chloride, V(\(^i\)OPr)\(_3\) is still hydrolytically sensitive under ambient conditions, thus our sol–gel reactions were performed at reduced temperatures (dry ice–ethanol bath, \(\sim\)72°C). In the present case, propylene oxide is added to an ethanolic solution of V(\(^i\)OPr)\(_3\) and Fe(III) chloride, resulting in robust VFe\(_2\)O\(_x\) gels that are ultimately processed into high surface-area, ultraporous aerogels.

**Characterization of VFe\(_2\)O\(_x\) aerogel structure and composition**

The as-synthesized VFe\(_2\)O\(_x\) aerogels comprise interpenetrating networks of through-connected solid and pores with feature sizes on the order of tens of nanometers, typical for aerogel-type materials (Fig. 1 and Fig. S1). The porous, nanostructured nature of this material is confirmed by N\(_2\)-sorption porosimetry, which shows specific surface area of 535 m\(^2\) g\(^{-1}\), cumulative pore volume of 1.6 cm\(^3\) g\(^{-1}\) (Table 1), and a wide distribution of pore sizes with an average of 13 nm (Fig. S2). As expected from a low-temperature sol–gel synthesis, the as-prepared VFe\(_2\)O\(_x\) aerogel is amorphous when examined by XRD.
The disordered, as-synthesized VFe$_2$O$_x$ aerogel was subjected to thermal processing under controlled atmospheres to tune the crystallinity of the VFe$_2$O$_x$ structure and to remove organic byproducts of the epoxide-driven reactions. Thermal analysis (simultaneous TGA and DSC) under flowing O$_2$ or Ar was performed to determine the lowest temperature necessary to transform and/or purify the as-synthesized VFe$_2$O$_x$ aerogel (Fig. S3). Under either atmosphere the VFe$_2$O$_x$ aerogel exhibits weight loss up to $\sim$27%, mostly occurring before 300°C; we attribute this weight loss to the volatilization of organic residues from the sol–gel synthesis.  

On the basis of these findings, we chose 300°C as our endpoint for thermal processing—a temperature sufficient to remove unwanted byproducts and to induce partial crystallization, but also mild enough to minimize particle ripening and concurrent loss of surface area. Following similar protocols reported earlier for FeO$_x$ aerogels, we also applied a two-stage treatment at 300°C, first under Ar to induce crystallization and then under O$_2$ to oxidize the metal sites in the VFe$_2$O$_x$ aerogels to obtain a more defective, $\gamma$-Fe$_2$O$_3$–like form. Elemental analysis of thermally processed VFe$_2$O$_x$ aerogels by EDS confirms that the 2:1 Fe:V stoichiometry from the initial synthesis is retained.

Oxidative heat treatment of the as-synthesized VFe$_2$O$_x$ aerogel partially densifies the networked structure while retaining the ultraporous morphology and broad pore-size distribution as determined by SEM, TEM, and N$_2$-porosimetry (Figs. 1, 2, and S2); total pore volume decreases $\sim$20% to 1.3 cm$^3$ g$^{-1}$ and the specific surface area is reduced to 231 m$^2$ g$^{-1}$ (Table 1). Heat treatment under low p$_{O_2}$ (300-Ar) also retains the ultraporous aerogel morphology (Figs. 2, S2, and S4) but further reduces surface area to 165 m$^2$ g$^{-1}$ and pore volume to 0.95 cm$^3$ g$^{-1}$ (Table 1). Subsequent oxidative heat treatment of the 300-Ar aerogel does not alter the pore-size distribution or surface area (Table 1 and Fig. S2). For comparison, a pure FeO$_x$ aerogel calcined to 300°C in O$_2$ has a higher surface area (416 m$^2$ g$^{-1}$) and a narrower pore-size distribution centered at 38 nm, in contrast to the broad distribution of mesopores observed for all VFe$_2$O$_x$ aerogels (Fig. S2).

The XRD-amorphous nature of the as-synthesized VFe$_2$O$_x$ aerogel is retained with calcination in high p$_{O_2}$ (300-O$_2$; Fig. 3), whereas heating to 300°C under inert atmosphere (300-Ar) produces a nanocrystalline cubic phase with peaks corresponding to either maghemite ($\gamma$-Fe$_2$O$_3$; ICDD# 00-039-1346) or magnetite (Fe$_3$O$_4$; ICDD# 01-073-9877). Further oxidative heat treatment of the nanocrystalline 300-Ar VFe$_2$O$_x$ aerogel induces a decrease in atomic order as evidenced by
broadened diffraction peaks, reduced peak intensity, and the appearance of a broad amorphous feature centered around 30°2θ (Fig. 3). Using Scherrer analysis of the (400) peak, the average crystallite sizes for the 300-Ar and 300-Ar-O2 samples are calculated to be 9.2 and 7.9 nm, respectively. The average crystallite sizes are comparable to the distribution of primary particle sizes (5–15 nm) observed by TEM (Fig. 2); the slightly larger particle size derived from TEM is attributed to partial atomic disorder in the particles, which will not contribute to the average crystallite size. Although we established crystallinity of the VFe2Ox materials by XRD, the phase and degree of order in the VFe2Ox nanoarchitectures can also be qualitatively accessed by color and magnetic susceptibility. The amorphous aerogels (as-synthesized and 300-O2–treated) are light brown and paramagnetic, whereas the nanocrystalline 300-Ar and 300-Ar-O2 aerogels strongly interact with a permanent magnet and are black and dark brown, respectively.

The magnetite and maghemite spinel phases are isostructural and therefore difficult to differentiate, particularly in nanocrystalline materials where diffraction peaks broaden. To further elucidate the crystalline phase for the 300-Ar and 300-Ar-O2 VFe2Ox aerogels, we used bright X-rays from a synchrotron source, combined with Rietveld analysis of the PXRD pattern (Fig. S5). We observe two phases in their diffraction profiles: (i) a nanocrystalline structure and (ii) an amorphous component (as evidenced by the presence of a large background despite the use of a synchrotron source). For Rietveld refinement, the ratio of Fe:V was fixed at 2:1 and it was assumed that vanadium occupy tetrahedral sites, as observed by Gillot and Nivoix for VxFe3−xO4 phases where x < 1;7 the amorphous component was accounted for with a ninth-order Chebyschev polynomial. When using the magnetite structure as a starting point, we obtain a better fit to the diffraction profile than when starting with the maghemite structure (see supporting information). We attribute the amorphous region at low 2θ to the disordered nature of aerogel surfaces and the large surface-to-bulk ratio present in these ultraporous oxide nanoarchitectures.

The relative diffraction peak intensities for (0,k,l) reflections are anomalously high for the 300-Ar VFe2Ox aerogel, as is the (0,4,4) peak intensity for the 300-Ar-O2 aerogel. These anomalies indicate that stacking faults are present within the crystalline component although fitting a model of the stacking faults to the PXRD is inhibited by the amorphous contribution to the profile and nanocrystalline peak broadening.38 This structure refines to a cubic unit cell with a = 8.33 Å and with coherent crystallite sizes of the 300-Ar and 300-Ar-O2 samples calculated to be 9.50 and
7.53 nm, respectively, in good agreement with the Scherrer analysis of diffraction profiles from XRD.

The oxidation states of V and Fe in the VFe\textsubscript{2}O\textsubscript{x} aerogels were assessed by deconvolving XPS regional spectra for V2p\textsubscript{3/2} (Fig. 4) and Fe2p\textsubscript{3/2} (Fig. S6). The 300-O\textsubscript{2} aerogel had a single V2p\textsubscript{3/2} peak at 517.7 eV, which corresponds to V\textsuperscript{5+} state.\textsuperscript{39} Spectra for the 300-Ar VFe\textsubscript{2}O\textsubscript{x} show two overlapping V2p\textsubscript{3/2} peaks at 517.2 and 516.1 eV that indicate a mixture of V\textsuperscript{5+} and V\textsuperscript{4+}, a result of partial reduction of V\textsuperscript{5+} sites during low-p\textsubscript{O}\textsubscript{2} heat treatment. Subsequent heating in O\textsubscript{2} (300-Ar-O\textsubscript{2}) returns the vanadium to +5, as indicated by a single V2p\textsubscript{3/2} peak at 517.3 eV. The Fe2p regions for the three VFe\textsubscript{2}O\textsubscript{x} aerogels consist of broad peaks that generally do not differ between the various heat treatments. The position of the Fe2p\textsubscript{3/2} satellite suggests that the predominant oxidation state is Fe\textsuperscript{3+}, but the peak for 300-Ar has a slightly lower binding energy at 719.4 eV, which indicates the presence of Fe\textsuperscript{2+}.\textsuperscript{40} The O1s spectra of all three samples are similar, and indicative of hydrated or defective oxides.

X-ray absorption spectroscopy was also performed on this series of VFe\textsubscript{2}O\textsubscript{x} aerogels, as well as analogous unsubstituted FeO\textsubscript{x} aerogels, to determine oxidation state and local structure. The XANES region includes contributions from dipole-allowed transitions from 1s states to unoccupied final states with p character (Figs. 5, S7, and S8). The pre-edge peak, however, is due to transitions from 1s states to final states with 3d character, which are forbidden by dipole selection rules but allowed by quadrupole selection rules. The intensity of quadrupole-allowed transitions is usually weaker than those of dipole-allowed transitions, as is the case for the Fe XANES (Figs. 5, S7, and S8).\textsuperscript{41} For vanadium oxides, the intensity of the pre-edge peak is significantly enhanced due to lack of centrosymmetry as a result of the high degree of distortion of the VO\textsubscript{6} octahedral geometry. The X-ray edge energy (at half-height beyond the pre-edge peak) and the pre-edge peak energy display a positive shift with increase in V oxidation state.\textsuperscript{42,43,44} The pre-edge peak intensity also increases with greater VO\textsubscript{6} octahedral distortion and to a lesser degree with increasing density of unoccupied d states that accompany higher V oxidation states.

The Fe oxidation state in the as-synthesized and 300-O\textsubscript{2} FeO\textsubscript{x} aerogel is close to +3; thermal treatment under Ar shifts the Fe oxidation state to ~+2.8 (Fig. S7). The VFe\textsubscript{2}O\textsubscript{x} aerogel samples also have Fe oxidation states that remain within a narrow window very close to +3 (2.94–3.12), with the lowest Fe oxidation state exhibited by the 300-Ar aerogel (Fig. 5a and Fig. S8).
agreement with XPS, the V K-edge XANES results indicate a +5 oxidation state for the as-synthesized VFe$_2$O$_x$ aerogel and for the aerogels treated under oxidizing environments (300-O$_2$ and 300-Ar-O$_2$), whereas the heating under low p$_{O_2}$ reduces the vanadium toward +4 (Fig. 5b and Fig. S8). However, an increase in pre-edge peak intensity indicates a greater degree of distortion in the 300-Ar VFe$_2$O$_x$ aerogel than that of the V$^{4+}$ standard, VO$_2$.

The local structure of the as-synthesized FeO$_x$ aerogel, as determined by EXAFS, is highly disordered, evidenced by a lack of significant contributions from higher coordination spheres in the region of the Fourier transform data above 2 Å (Fig. S9). Disorder decreases following calcination at 300°C in O$_2$ as evidenced by the increase in the amplitude of the structure in the 2.2–3.6 Å region of the Fourier transform. Thermal treatment in Ar induces significant changes, particularly in the first coordination sphere (Fe–O peak centered at ~1.5 Å in the Fourier transforms data) of FeO$_x$, resulting in a local structure that is closely related to γ-Fe$_2$O$_3$ (maghemite), especially in the region dominated by Fe–Fe interactions (2.2–3.6 Å region). The shift in the Fe–O peak to slightly higher distance is consistent with the presence of a small fraction of Fe$^{2+}$ as a result of heating in Ar. The local structure of Fe in VFe$_2$O$_x$ is similar for the as-synthesized, 300-O$_2$, and 300-Ar-O$_2$ aerogels, and may be interpreted as a disordered form of γ-Fe$_2$O$_3$ (Fig. 6 and Fig. S10). The local structure of V for VFe$_2$O$_x$ heated to 300°C in Ar is clearly distinct from the structure that emerges under oxidative conditions (Fig. 6 and Fig. S11). The increase in the amplitudes of the structure in the 2.2–3.6 Å region of the Fourier transforms of the EXAFS spectra indicates that the 300-Ar VFe$_2$O$_x$ aerogel exhibits a more ordered form related to γ-Fe$_2$O$_3$.

Based on the synchrotron PXRD, EXAFS, and TEM results, we posit that our material consists of domains of nanocrystalline magnetite-like and amorphous, maghemite-like oxide, similar to our previous assessment of FeO$_x$ aerogels that showed mixed magnetite/maghemite character. This broad, amorphous PXRD pattern has previously been observed for core–shell maghemite/magnetite FeO$_x$ nanoparticles.

**Electrochemical cation-insertion as a function of structure and composition**

We use these VFe$_2$O$_x$ and FeO$_x$ aerogels as model electrode materials with which to investigate the influence of structural order/disorder, cation-vacancy content, and V substitution on electrochemical charge-storage properties, focusing primarily on Li$^+$-insertion reactions in nonaqueous electrolytes. Cyclic voltammetry (CV) provides an initial assessment of capacity and
active potential window, as seen when VFe$_2$O$_x$ or FeO$_x$ aerogel powders are processed into conventional composite electrodes and cycled at 0.5 mV s$^{-1}$ in a three-electrode cell (Fig. 7). In all cases, most of the capacity is delivered between 3.2 and 2.0 V vs Li, with broad voltammetric profiles reminiscent of pseudocapacitive processes.

Integration of the voltammograms to obtain capacity values shows that the 300-O$_2$ VFe$_2$O$_x$ aerogel provides the highest specific capacity of the series, reaching 130 mA h g$^{-1}$. The impact of V substitution on electrochemical performance is clear when compared to an analogously processed FeO$_x$ aerogel, which delivers only 60 mA h g$^{-1}$. The ideal stoichiometry for these respective oxides in their fully oxidized, cation-defective forms is [Fe$^{3+}$]$^{8/3}$·□$^{1/3}$O$_4$ and [V$^{5+}$]$^{8/11}$Fe$^{3+}$]$^{16/11}$·□$^{9/11}$O$_4$, with greater vacancy content for V-substituted FeO$_x$ due to the need for additional charge compensation when V$^{5+}$ replaces Fe$^{3+}$ in the spinel lattice. Assuming a 1:1 correlation between vacancy content and Li-ion capacity, and accounting for the difference in formula mass, VFe$_2$O$_x$ should provide 2.90 times the specific capacity of an analogous cation-defective FeO$_x$ material; experimentally, we observe capacity improves by a factor of 2.17.

Heating the as-synthesized VFe$_2$O$_x$ aerogel directly in Ar produces a nanocrystalline and partially reduced form that exhibits much lower specific capacity (77 mA h g$^{-1}$) than the poorly crystalline, 300-O$_2$ aerogels. The diminished capacity expressed by 300-Ar VFe$_2$O$_x$ is recovered by $\sim$35% to 105 mA h g$^{-1}$ after subsequent heating in O$_2$, which oxidizes all V to the +5 state and creates more cation vacancies, while also increasing overall structural disorder, all without altering specific surface area or pore structure. However, the fully oxidized, nanocrystalline 300-Ar-O$_2$ VFe$_2$O$_x$ still does not achieve the Li-ion capacity of the X-ray-amorphous 300-O$_2$ analog. The difference in specific surface area (230 vs. 160 m$^2$ g$^{-1}$) for these two VFe$_2$O$_x$ aerogels may play a role in establishing Li-ion capacity, as vacancies and defects are favored at surface sites. Similar trends are also observed for VFe$_2$O$_x$ cycled in a Na-ion electrolyte, albeit achieving a lower total capacity due to the larger size of the Na$^+$ cation (Fig. 7); VFe$_2$O$_x$ 300-O$_2$ yields 70 mA h g$^{-1}$ in Na$^+$ electrolyte compared to 130 mA h g$^{-1}$ in Li$^+$ electrolyte.

The oxygen-calcined, X-ray-amorphous VFe$_2$O$_x$ aerogel was selected for galvanostatic cycling experiments (at 10 mA g$^{-1}$) in Li coin cells. Representative charge–discharge profiles are shown in Fig. 8a; the sloping nature of these curves is consistent with the broad shapes observed in the voltammetric tests. Capacity values were also derived from these galvanostatic experiments, returning 186 mA h g$^{-1}$ and 157 mA h g$^{-1}$ on first and second discharge, respectively; the capacity
drop in this case is likely due to solid electrolyte–interface (SEI) formation. Thereafter, capacity fades gently with specific capacity maintained at \(~100\ \text{mA h g}^{-1}\) through 50 cycles. Charge–discharge coulombic efficiency ranges between 87–89% over the 50 cycles examined, which may indicate parasitic side reactions occurring during charging or some incremental irreversibility in the Li\(^{+}\)-insertion process. Further work is underway to enhance cycling stability, understand SEI formation, and further amplify specific capacity in this new class of cation-insertion materials.

**Conclusions**

Using a combined strategy of cation-substitution and nanostructuring, we synthesize deliberately defective VFe\(_2\)O\(_x\) aerogels and demonstrate that increasing concentrations of cation vacancies concomitantly enhances their specific capacity for Li\(^{+}\) and Na\(^{+}\)-insertion. Aerogel frameworks create a defect-rich structure with high accessibility to the defect sites, and the substitution of tetrahedral iron sites with V\(^{5+}\) induces further vacancy formation. We observe the highest specific capacity (130 mA h g\(^{-1}\)) in Li\(^{+}\)-containing electrolyte when the VFe\(_2\)O\(_x\) aerogel is calcined in oxidizing atmospheres such that high surface area is retained and the X-ray amorphous oxide expresses \(\gamma\)-Fe\(_2\)O\(_3\)–like local structure.

**Acknowledgements**

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**TABLE 1:** Brunauer–Emmett–Teller (BET) surface areas, Barrett–Joyner–Halenda (BJH) pore volumes, and specific discharge capacities for select VFe$_2$O$_x$ and FeO$_x$ aerogels

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$ g$^{-1}$)$^a$</th>
<th>BJH pore volume (cm$^3$ g$^{-1}$)</th>
<th>discharge capacity in Li$^+$-electrolyte (mA h g$^{-1}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VFe$_2$O$_x$ as-synthesized</td>
<td>535</td>
<td>1.6</td>
<td>n/a</td>
</tr>
<tr>
<td>VFe$_2$O$_x$ 300-O$_2$</td>
<td>231</td>
<td>1.3</td>
<td>130</td>
</tr>
<tr>
<td>VFe$_2$O$_x$ 300-Ar</td>
<td>165</td>
<td>0.95</td>
<td>77</td>
</tr>
<tr>
<td>VFe$_2$O$_x$ 300-Ar-O$_2$</td>
<td>156</td>
<td>0.87</td>
<td>105</td>
</tr>
<tr>
<td>FeO$_x$ 300-O$_2$</td>
<td>416</td>
<td>2.3</td>
<td>60</td>
</tr>
</tbody>
</table>

$^a$ Values are ±2% for replicate analyses within batch and ±10% for batch-to-batch analysis

$^b$ Capacities derived by integration of voltammetric curves at 0.5 mV s$^{-1}$ scan rate.
Figure 1

Fig 1  Scanning electron micrographs of VFe$_2$O$_x$ aerogels: (a) as-synthesized an (b) 300-O$_2$. 
Figure 2

Transmission electron micrographs of VFe$_2$O$_x$ aerogels: (a) as-synthesized, (b) 300-O$_2$, (c) 300-Ar, and (d) 300-Ar-O$_2$.

Figure 3

**Fig 3** X-ray diffraction profiles of VFe$_2$O$_x$ aerogels: 300-O$_2$ (—), 300-Ar (—), and 300-Ar-O$_2$ (—). Diffraction peaks for 300-Ar and 300-Ar-O$_2$ index to either maghemite ($\gamma$-Fe$_2$O$_3$; ICDD# 00-039-1346) or magnetite (Fe$_3$O$_4$; ICDD# 01-073-9877).
Figure 4

Fig 4 X-ray photoelectron spectra of the V\textsubscript{2p\textsubscript{3/2}} binding energy for VFe\textsubscript{2}O\textsubscript{x} aerogels: 300-O\textsubscript{2} (—), 300-Ar (—), 300-Ar-O\textsubscript{2} (—), background fit (— — —), and peak fit (— — —).
Figure 5

(a) V K-edge and (b) Fe K-edge XANES for VFe$_2$O$_x$ aerogels: 300-O$_2$ (---), 300-Ar-O$_2$ (---), 300-Ar (---), and as-synthesized (•••).
**Figure 6**

Fourier transform plots of (a) V and (b) Fe K-edge EXAFS spectra for VFe$_2$O$_x$ aerogels: 300-O$_2$ (---), 300-Ar-O$_2$ (-- -), 300-Ar (--- -), and as-synthesized (•••).
Figure 7

![Cyclic voltammograms for composite cathodes in Li⁺ and Na⁺ containing electrolytes.](image)

**Fig 7** Cyclic voltammograms at 0.5 mV s⁻¹ of composite cathodes prepared with (—) VFe₂Oₓ 300-O₂, (— — —) VFe₂Oₓ 300-Ar-O₂, (— • • •) VFe₂Oₓ 300-Ar, and (• • •) FeOₓ 300-O₂ in (a) Li⁺-containing electrolyte and (b) Na⁺-containing electrolyte.
Figure 8

Fig 8 (a) Galvanostatic charge–discharge cycling of a 300-O$_2$ VFe$_2$Ox aerogel at 10 mA g$^{-1}$ between 4.0 and 2.0 V vs. Li in 1 M LiPF$_6$ in 1/1/1 EC/DEC/DMC; (b) discharge capacity versus cycle number for the galvanostatic cycling.
Notes and references

† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/


VFe$_2$Ox aerogel architectures are synthesized such that cation-vacancy formation is enhanced by their high surface area and substituting a fraction of the Fe$^{3+}$ sites for high-valent V$^{5+}$; increased capacity for Li$^+$- and Na$^+$-insertion, approaching 130 mAh g$^{-1}$ and 70 mAh g$^{-1}$, respectively, is correlated with a larger concentration of cation vacancies and structural disorder.