

Exploiting cation vacancies in nanocrystalline metal oxides for electrochemical charge storage

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Cation-inserting transition metal oxides are a key class of materials for electrochemical energy storage, being used as active electrodes in devices ranging from Li-ion batteries to electrochemical capacitors. Such materials are often designed and characterized as well-defined crystalline forms, but the deliberate incorporation of particular structural defects, namely cation vacancies, can enhance performance in terms of total cation-insertion capacity or potential, while still maintaining relatively simple and low-cost electrode compositions (e.g., manganese and iron oxides).¹ The benefits of cation vacancies were initially described by Reutschi in the mid-1980s for proton-insertion into δ -MnO₂,^{2,3,4} but the extension of this concept to other systems has been limited until recently.

Maghemite (γ -Fe₂O₃) is a naturally occurring mineral that contains cation vacancies dispersed in a spinel crystal structure. Synthetic versions of γ -Fe₂O₃, particularly when expressed in nanoscale forms, demonstrate enhanced Li-ion storage properties relative to other iron oxides, with additional Li-ion capacity and more positive electrode potential attributed to the presence of cation vacancies.^{5,6,7} We are also exploring spinel iron oxides as cation-insertion materials, but focus on ultraporous, high-surface-area aerogel forms that should further amplify the effects of cation vacancies.⁸ Iron oxide (FeOx) aerogels are synthesized via sol-gel chemistry using epoxides to drive the hydrolysis/condensation of iron salts in alcohol solutions.⁹ Low-density, monolithic FeOx aerogels are produced following gelation, rinsing, and supercritical-CO₂ extraction. The as-prepared FeOx aerogel exhibits high-surface-area (400–600 m² g⁻¹), and is amorphous by X-ray diffraction.

Iron oxide aerogels provide a model system with which to investigate the role of structural order/disorder on cation-insertion reactions, as the degree of crystallinity and cation vacancy content can be varied by heating the amorphous as-prepared FeOx in a controlled atmosphere.¹⁰ For example, calcination in air to 260°C yields a poorly crystalline material with hints of a spinel structure by XRD, while heating under low O₂ partial pressure (flowing argon) produces a clearly nanocrystalline FeOx with a spinel structure that is consistent with either maghemite or magnetite (Fe₃O₄). Raman scattering provides complementary information by which we are able to identify the presence of cation vacancies in FeOx aerogels that have been heated in air, either direct heating of the as-prepared aerogel or by subsequent calcination of an argon-heated aerogel.¹¹ In all cases, the structural characteristics of an aerogel are maintained—high specific surface area, through-connected

porosity in the mesopore size regime, and bonded networks of oxide nanoparticles.

Electrochemical assessment of FeOx aerogels is performed by fabricating conventional powder-composite electrodes with carbon powder and polymer binder and assembled into coin cells with Li foil anodes and a carbonate-based electrolyte. Cyclic voltammetry reveals a pseudocapacitive signature for the FeOx aerogels that is not uncommon for nanoscale and/or disordered/defective metal oxides. Galvanostatic charge-discharge measurements demonstrate the partially crystalline, cation-deficient FeOx aerogel exhibits the highest capacity (~100 mA h g⁻¹) and good cycling stability.

The electrochemical performance of iron oxides can be further improved by increasing the vacancy content beyond the theoretical 0.33 vacancies-per-formula-unit for γ -Fe₂O₃. This goal can be achieved synthetically by substituting highly oxidized cations (Mo⁶⁺, V⁵⁺) for a fraction of the Fe sites in the spinel FeOx framework. Additional cation vacancies form within the lattice to compensate for the positive charge of the substituent metal.¹¹ We recently demonstrated that Mo-substituted nanocrystalline ferrites, synthesized via base-catalyzed hydrolysis from aqueous solutions, exhibit vacancy fractions that are 2–3 times greater than the theoretical for γ -Fe₂O₃, resulting in Li-ion insertion capacities for the Mo-FeOx spinel ferrite that exceed 100 mA h g⁻¹, compared to 20 mA h g⁻¹ for similarly synthesized nanocrystalline γ -Fe₂O₃ precipitates.¹² We are now combining this metal substitution strategy with aerogel synthesis to obtain the benefits of both approaches for maximizing cation vacancy content and corresponding electrochemical performance. We are also exploring this class of defective oxides as ion-insertion hosts for such alternative cations as Mg²⁺.

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