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 in 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 vacancies.2–4 limited until recently.

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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 aim goal can be achieved synthetically by substitutional highly oxidized cation (Mo⁵⁺, 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 nanocristalline 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 mAh g⁻¹ compared to 20 mAh g⁻¹ for comparably synthesized nanocristalline 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 Mg⁶⁺.13

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 pseudo-capacitive 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 mAh g⁻¹) in combination with good cycling stability.

References