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Rechargeable Fe(III/VI) super-iron cathodes

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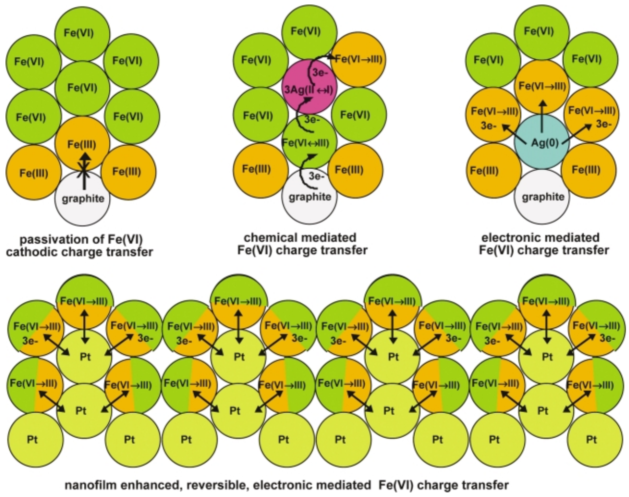
This study addresses a fundamental challenge posed by hexavalent iron electrochemical irreversibility, which had slowed practical development of reversible Fe(VI) cathodes; nanolayers circumvent fundamental passivation challenges, and are electrodeposited from solution phase FeO$_4^{2-}$, forming 601 mAh g^{-1} Li, and 485 mAh g^{-1} Na, Fe(III/VI) alkaline cathodes, the latter exhibiting 100–200 storage cycles at 80% depth of discharge, providing pathways towards metal hydride batteries with twice the cathode capacity.

Compared to other cathode materials, the energetic, yet non-toxic character of Fe(VI) salts, has led to a focused attention on the electrochemistry of these novel materials.[1–3] Here, we report a first demonstration of extended reversibility of the Fe(III/VI) redox couple. Contemporary, widely used metal hydride batteries, have a capacity of over 95 Wh kg^{-1},[4] compared to 40 Wh kg−1 for NiCd batteries. Energy improvements in these rechargeables is largely limited by the cell's heavy nickel oxyhydroxide cathode, with a 290 mAh g^{-1} cathode capacity. Fe(VI) salts have been probed as oxidants for synthesis and water purification.[5] Since their 1999 introduction for energetic batteries in both aqueous and non-aqueous environments,[1] we have synthesized, characterized, and electrochemically probed a variety of Fe(VI) cathodes.[8–10] Incremental progress of Fe(VI) cathodes includes activation of the stable Fe(VI) salt, K$_2$FeO$_4$,[6] graphite mix[7a] and nonaqueous advances,[7b] and recent syntheses of stabilized BaFeO$_4$.[7c]

We attribute prior observations of only 1F reversible cathodic storage per Fe(VI),[1,8b] to conductivity constraints imposed by the ferric oxide product of reduced Fe(VI), as illustrated in the upper left of Scheme 1. Fe(VI) cathode passivation[8c] has led to exploration of alternate pathways to facilitate primary Fe(VI) charge transfer. As illustrated in the center of Scheme 1, Mn(VII), with an alkaline oxidation potential near lying to the Fe(III/VI) redox couple, was observed to chemically mediate and improve sustainable Fe(VI) charge transfer, by displacing the passivating Fe(III) sites away from the conductive matrix of the substrate.[6a] This improved the extent of the Fe(VI) reduction, but did not improve reversible charge transfer. This challenge persisted and a recent study, again reported a maximum reversibility of approximately only 30% DOD (depth of discharge of the three Faraday capacity).[10c] That study provided useful Mössbauer evidence that the 1F reversible cathodic discharge product was a mix of Fe(III) and passivated Fe(VI) salts, rather than an intermediate valence state iron. Ag(II) interspersed in the Fe(VI) cathode mix led to an unusually energetic discharge in the problematic high power domain.[6b] As represented in the right of Scheme 1, this is consistent with an additional electronic mediation of Fe(VI) charge transfer, in which the reduced mediation center itself extends, the conductive matrix; better interaction with the conductive substrate will improve cathodic Fe(VI) charge transfer and cycling.



Scheme 1 Modes of Fe(VI) charge transfer passivation and activation.

Chemical and electrochemical synthesis forms Fe(VI) salts that are chemically similar.[7c] New results, Fig. 1, indicate that the grain size of the latter is substantially smaller, a morphology conducive to charge transfer. As illustrated in the lower portion of Scheme 1, in principle, a sufficiently thin film Fe(III/VI) cathode should facilitate electronic communication with a conductive substrate to sustain cycled charge storage or reversible deposition. However, a variety of Fe(VI) thin films, formed by pressure and/or mix with a granular conductor such as small grain carbons,[10c] had passivated upon charge cycling. We now observe that rechargeable ferric films can be generated, formed by electrodeposition onto conductive substrates from solution phase Fe(VI) electrolytes. Fe(VI) salts are highly insoluble in organic solvents, and saturated and Ba(OH)$_2$ KOH solutions,[8a,e,10a] but the Fe(VI) species, FeO$_4^{2-}$, is significantly soluble in solutions including 10 M NaOH and 5 M LiOH.[1,9b]

A thin film, conducive to Fe(VI) charge cycling, is generated from micro-pipette controlled, microliter volumes of dissolved Fe(VI) in alkaline solution. The solution is placed on a Pt foil electrode, and isolated (by cation selective, alkali resistant, Nafion 350 membrane) from a larger volume, which contains an immersed reference electrode and a Pt gauze counter electrode in alkaline solution. Fig. 2 presents two representative examples of the cathode formation, including deposition of either a 410 or 110 nm film, each with a surface area of 0.3 cm^2 on Pt foil, and with respective film thicknesses of approximately 0.8 μm and 0.2 μm. As illustrated in the bottom and top of the figure, either potentiostatic, or galvanostatic depositions approach 100% coulombic efficiency. The potentiostatic process for cathode film formation is preferred, as the galvanostatic deposition necessitates multiple constant current steps, and longer time for film completion. The film may be cycled *in-situ*, or removed, and washed with de-ionized water, and returned to the cell. We have observed that the film is also equally active, whether formed from a solution containing dissolved,

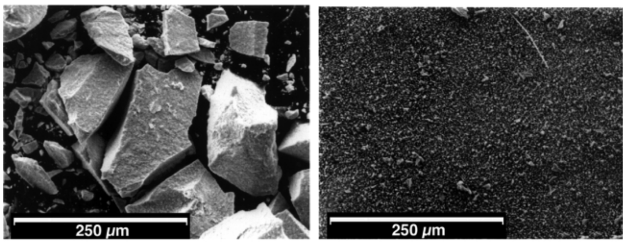


Fig. 1 SEM of chemical (left) and electrochemical (right) synthesized[7c] BaFeO$_4$. Grain size is stable before and after 45 °C, 30 day storage.

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chemically synthesized Fe(VI) salts, or an electrochemically formed solution[7c] of dissolved Fe(VI). The choice of alkaline Fe(VI) solution (*e.g.* Li_2FeO_4, Na_2FeO_4 or K_2FeO_4, in LiOH, NaOH or KOH) and concentration, permits variation of the thickness and composition of the generated film.

Whereas a one micron Fe(III/VI) layer, deposited on Pt foil by this technique, can support >1000 reversible charge/discharge cycles to 30% DOD, the film passivates within several cycles at deeper discharge levels. However a thinner film delays the onset of passivation. A 0.1 μm Fe(VI) film sustains 200 cycles of 50% DOD, or 20 cycles of deeper (80%) DOD, after which the film passivates. We observe that a nanofilm (for example, a 3 nm thickness Fe(VI) film), formed by the same technique is highly reversible. This Fe(III/VI) film on Pt foil is formed by reduction of 5 mM Na_2FeO_4 in 10 M NaOH at 100 mV *vs.* Ag/AgCl, followed by film inspection and galvanostatic cycling. The film is rigorous, and when used as a storage cathode, exhibits charging and discharging potentials characteristic of the Fe(VI) redox couple, and extended, substantial reversibility.

Fig. 3 presents the first reported measurements of a three Faraday capacity, reversible Fe(III/VI) cathode. As seen in the figure, a full 80% DOD of the 485 mAh g^{-1} capacity Na_2FeO_4 film is readily evident after 100 galvanostatic cycles. The nano-thick layers promotes the reversible charge transfer, and a full 80% discharge is still attained by the 200th cycle (not shown), although the charging potential is observed to increase during cycling, and by this cycle an overpotential of 1 V is needed to complete the charge. In thicker films, the cycle failure had been due to a decrease in cathode capacity, as evidenced by the onset of an anodic shift in polarization during discharge. This compares to the thinner films in which the number of deep discharge cycles is extended, and the eventual cycle failure is not due to a decrease in capacity, but rather to the observed increase in charging potential. Improved electronic contact to the conductive substrate can decrease this effect, related to competing O_2 co-evolution during the charging process.[10b] We will be exploring the use of Pt black and porous metal substrates to further extend the thickness and cycling of the Fe(VI) cathode.

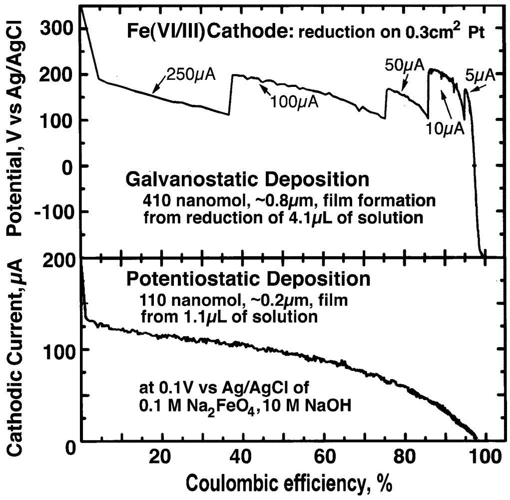

Fig. 2 Electrochemical, galvanostatic or potentiostatic deposition of a thin Fe(VI/III) film onto Pt foil. Coulombic efficiency is integrated current during the deposition, normalized to the 3F available 0.1 M Fe capacity.

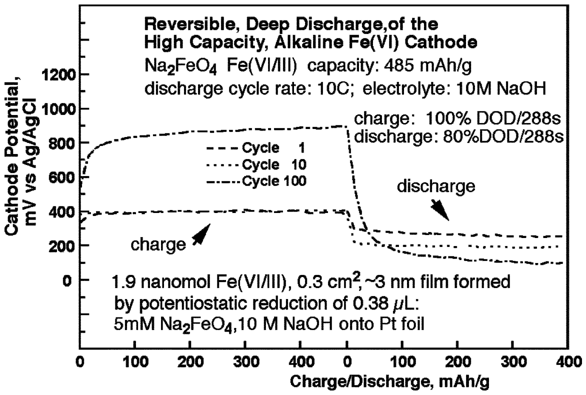

Fig. 3 Reversible charge storage of a Fe(VI) of a 485 mAh g^{-1} capacity Na_2FeO_4 nanofilm. Each galvanostatic storage cycle is 100% DOD charge followed by 80% DOD discharge, at the 10 C discharge rate.

We observe that the reversible Fe(III/VI) film cathode exhibits a potential near, but somewhat greater (0 to 150 mV more positive) than the NiOOH cathode, providing a higher capacity alternative for NiOOH used in metal hydride batteries. We observe a cathodic shift in the Fe(III/VI) potential in both NaOH and LiOH, compared to equal concentration KOH electrolytes. Hence, the cathodic potential can be "tuned" with the choice of alkaline electrolyte. The aqueous solubility of LiOH, 5 molal, is considerably less than that of NaOH. This is observed to make deposition of a reversible lithium Fe(III/VI) film more challenging, presumably due to the diminished stability of $FeO_4{}^{2-}$ in lower concentrations of hydroxide.[1] Initial results of a higher capacity lithium Fe(VI) cathode are promising, although presently such cathodes are less reversible than the Na_2FeO_4 cathode. To date, 80% DOD cycling of the film's 601 mAh g^{-1} has been achieved through 15 cycles (after which substantial polarization losses are observed). Film integrity was determined by SEM/EDS, and thickness and composition redundantly by SEM/EDS, Faradaic and ICP analysis. Studies are underway to probe the thickness and composition variation upon cycling, as well as reversibility of these novel films in non-aqueous, lithium ion compatible, electrolytes. The light formula weight of Li_2FeO_4 (133.8 g $mole^{-1}$), provides a higher intrinsic (theoretical in mAh g^{-1}) 3 F cathodic capacity (601) compared to Na_2FeO_4 (485), K_2FeO_4 (406), $SrFeO_4$ (388) or $BaFeO_4$ (313).

This study provides a fundamental step towards a reversible, higher capacity, environmentally benign cathode, in an electrolytic environment compatible with new higher energy metal hydride storage batteries. Along with the principal advantage of demonstrated reversibility, the ultrathin (nanolayer) Fe(III/VI) salt films have the additional advantage of the direct formation of the desired solid cathode product.

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