

Nanosheets Deliver Great Power Density

This report features the work of Yan-Gu Lin and his co-workers published in Small 10, 3803 (2014).

The tremendous development of portable electronics and hybrid electric vehicles has led to urgent and increasing demand for high-energy storage devices. In recent years, much research effort has been undertaken to develop more efficient devices such as supercapacitors (SC), batteries and fuel cells for this purpose. In particular, electrochemical capacitors (EC), known also as pseudocapacitors, are gaining great popularity because of their ability to store energy, with the advantage of delivering the stored energy much more rapidly than batteries and fuel cells—implying power density. To become primary devices for power supply, SC must be developed further to improve their ability to deliver high energy and power simultaneously. For this reason, much effort is devoted to the investigation of pseudocapacitive transition-metal-based oxides and hydroxides and mixed metal oxides and hydroxides, mainly because they can produce much greater specific capacitances than typical carbon-based electric double-layer capacitors and electrically conducting polymers.

The rational design of nanoarchitectures with specific functions is a key requisite to increase the energy and power density of electrical storage systems. Energy extracted from the electrode material depends strongly on the textural and morphological effects at the interface between electrolyte and material. Recent reports have emphasized the relation between structure and activity of the electrode material that accentuates the importance of the surface morphology on the charge storage performance.¹ Charge storage is well known to involve an insertion or extraction of protons or ions in the first few nanometers at the surface of electrode materials for pseudocapacitors. Iron oxyhydroxide lepidocrocite (γ -FeOOH) with open two-dimensional (2D) permeable channels might be favorable for EC, as scientists recently described birnessite-type MnO_2 with layered nanostructures to facilitate ion transport and to ex-

hibit excellent capacitive performance.² In particular, the 2D layered structure with satisfactory interlayer conductivity of γ -FeOOH might greatly benefit EC. The design of anode materials based on γ -FeOOH with layered characteristics is expected to be an ideal microstructural solution to decrease the diffusion length of ions, to increase the contact area with electrolyte and to improve active material utilization, which enhances the electrochemical performance. A research team led by Yan-Gu Lin (NSRRC), Yu-Kuei Hsu (National Dong Hwa University) and Li-Chyong Chen (National Taiwan University) has cooperatively developed γ -FeOOH nanosheet (NS) anodes with distinct layered channels to improve electrochemical performance.³ The proposed NS-structure of γ -FeOOH on carbon cloth is depicted in Figs. 1(a) and 1(b). Novel γ -FeOOH NS were prepared via a simple one-step electroplating route without assistance of template or surfactant. The need of binder or conducting additive, which adds contact resistance and mass, becomes eliminated in this case.

To elucidate the mechanism of energy storage and the variation of oxidation state of the active metal of the γ -FeOOH NS electrode during charge and discharge cycles, synchrotron-based X-ray absorption spectra (XAS) were recorded *in situ* at BL17C1 of the TLS. X-ray absorption near-edge structure (XANES) spectra of γ -FeOOH NS electrodes *in situ* are presented in Fig. 1(c). Although the variation of shape of all spectra is slight, a clear shift of energy of the adsorption signal, toward greater energy with applied potential, is recognizable. The absorption threshold energy (E_0) is linearly correlated with the oxidation state of Fe in the γ -FeOOH NS electrodes (Fig. 1(d)). According to E_0 derived from the XANES spectra during charge and discharge cycles *in situ*, the average oxidation state of Fe in γ -FeOOH NS electrodes was determined in the sequence shown in Fig. 1(e). The results clearly confirm a large electronic

and ionic conductivity of the γ -FeOOH NS electrode in Li_2SO_4 electrolyte and a continuous and reversible faradaic redox transition of γ -FeOOH NS. Figure 1(f) shows the Fourier-transformed (FT) magnitude of Fe K-edge EXAFS spectra of the γ -FeOOH NS electrode in Li_2SO_4 electrolyte measured at several potentials in a sequence. The first FT maximum about 1.5 Å is attributed to an interaction of central Fe atoms with six coordinated oxygen atoms in the first coordination shell (i.e. Fe-O bond within a $[\text{FeO}_6]$ octahedral unit). The second FT maximum located near 2.7 Å corresponds to the nearest Fe atoms between neighboring $[\text{FeO}_6]$ octahedral sites (i.e. Fe-Fe interatomic distance between neighboring $[\text{FeO}_6]$ units). The interatomic distance of the Fe-O bond progressively decreases with applied potential increased from -0.8 to -0.1 V, originating from an oxidation from Fe^{2+} to Fe^{3+} . A decreased Fe-Fe distance was concurrently observed, indicating that the $[\text{FeO}_6]$ octahedral units contract. In this case, Li^+ is the primary working species that can intercalate into the 2D layered channels between the $[\text{FeO}_6]$ units; the Fe-Fe distance would be expected to increase. In contrast, oxidation of the electrode led to a clearly decreased Fe-Fe distance, which is attributed to the desertion of Li^+ from the γ -FeOOH NS structure. In a Li^+ operative electrolyte, both Fe-O and Fe-Fe signals shift in the same direction, toward larger Fe-O and Fe-Fe interatomic distances upon lithiation and back to smaller distances upon delithiation. As noted in Fig. 1(f), the intensity of the FT Fe-O maximum increases with applied potential increasing from -0.8 to -0.1 V. This result indicates that the relief of distortion in γ -FeOOH NS under deintercalation might restore a symmetric oxygen distribution in a $[\text{FeO}_6]$ octahedral unit. The redox transition during rapid charge and discharge cycling is hence charge-compensated by the reversible insertion and desertion of Li^+ into and from 2D layered channels between the $[\text{FeO}_6]$ octahedral units. Accordingly, a pseudocapacitive mechanism of the γ -FeOOH NS electrode, based on Li^+ as working ion in the

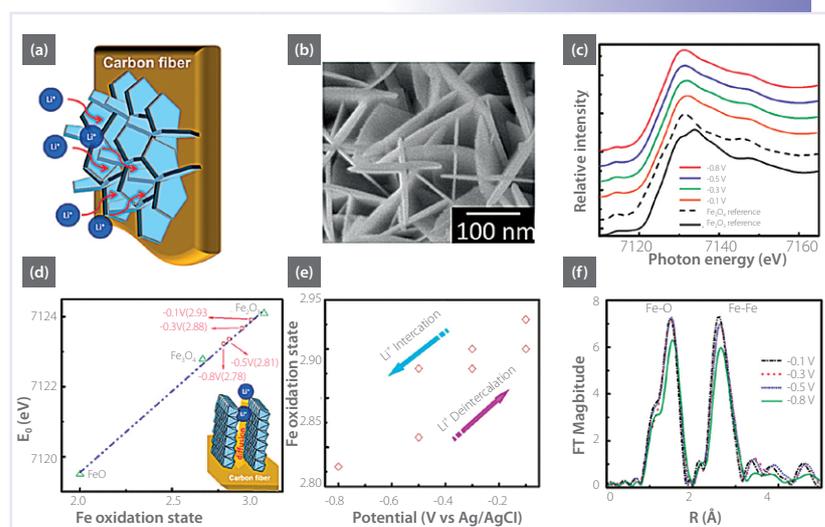


Fig. 1: (a) and (b): Scheme and SEM image of γ -FeOOH on carbon cloth, respectively. (c) Fe K-edge XANES spectra of the γ -FeOOH NS electrodes *in situ* in Li_2SO_4 electrolyte with applied potential increasing from -0.8 to -0.1 V. (d) Relation between edge position and Fe average oxidation state for γ -FeOOH NS electrodes at varied applied potentials. (e) Variation of Fe oxidation state with respect to applied potential. (f) Fe K-edge EXAFS spectra of the γ -FeOOH NS electrodes *in situ* in Li_2SO_4 electrolyte with applied potential increasing from -0.8 to -0.1 V. (Reproduced from Ref. 3)

Li_2SO_4 electrolyte, was proposed: $\text{Fe(III)OOH} + \text{Li}^+ \leftrightarrow \text{LiFe(II)OOH}$.

An efficient energy-storage system was developed based on layered γ -FeOOH NS anodes. The microstructural influence on pseudocapacitive performance of the obtained γ -FeOOH NSs was systemically investigated via XAS *in situ*. These results regarding mechanisms of charge storage in electrodeposited γ -FeOOH NS show that Li^+ can reversibly insert into or desert from the 2D channels between the $[\text{FeO}_6]$ octahedral subunits, depending on the applied potential. This process charge-compensates the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox transition upon charging and discharging, and thus contributes to an ideal pseudocapacitive behavior of the γ -FeOOH electrode. The work demonstrated here provides insight into the design and optimization of high-performance pseudocapacitors.

References

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