Iron oxide nanoconfined in carbon nanopores as high capacity anode for rechargeable alkaline batteries

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\textbf{ABSTRACT}

Rechargeable aqueous batteries are attracting renewed attention due to flammability and high cost of lithium-ion cells. Extremely low cost, very high abundance and eco-friendliness of iron (Fe) anodes make them particularly attractive for aqueous chemistries. Unfortunately, traditional Fe anodes suffer from low capacity utilization, the need for formation pre-cycling and dissolution of active material when fully discharged. Known methods for synthesis of nanocomposite Fe anode are expensive and offer poor control over material properties and uniformity. We report on a novel low-cost synthesis route to produce nanocomposites with crystalline FeO\textsubscript{x} nanoparticles very uniformly distributed within individual nanoporous carbon particles. The conductivity enhancement and a very small size of FeO\textsubscript{x} particles (< 5 nm) effectively enhance the discharge capacity of Fe anodes up to 600 mAh g\textsuperscript{-1}. In contrast to graphene-FeO\textsubscript{x} or carbon nanotube-FeO\textsubscript{x}, the large size of the produced nanocomposite particles allows them to be processed into electrodes the same way as supercapacitor electrodes are mass-produced by industry. The nanofeconfinement suppresses side reactions, such as nannoFe dissolution and hydrogen evolution, resulting in capacity retention of up to ~85% after 200 cycles. When used in combination with novel In-based additives, reported anodes uniquely exhibited a single high-voltage discharge profile in full cells, which improves energy density of cells and simplifies battery management system.

\section{1. Introduction}

Rapidly increasing demands of renewable energy harvesting (such as solar, wind) and growing market of electric vehicles has promoted increasing demand for high performance rechargeable batteries that have high energy density and power density and which are cost-effective and environmentally friendly [1–4]. Commercial Li-ion batteries (LIBs) utilize organic electrolytes, which exhibit high flammability. In addition, such batteries require expensive and relatively rare lithium (Li) and are mostly based on cobalt (Co) – containing cathodes. A recent study showed that Co-containing LIBs that additionally utilize solvent-based electrode processing and are based on organic electrolytes have multiple significant negative environmental impacts [5]. The production, processing, and use of cobalt, which may cause adverse respiratory, pulmonary, and neurological effects in those exposed [6]. The insufficient use of suitable personal protection equipment in many Co mining developing countries and recent findings of major exploitations of children in Co mines and the related child sickness and deaths [7,8] require an urgent search for safer, cheaper and more abundant battery chemistries. Iron (Fe) - based electrodes (similar to those used in century-old Ni/Fe batteries co-invented by Waldemar Jungner and Thomas Edison in the 1890s [9,10]) attract renewed interest due to extremely low cost, very high abundance and eco-friendliness of Fe as well as due to the compatibility of such electrode chemistry with nonflammable, low-cost aqueous alkaline electrolytes which exhibit high conductivity and thus do not require very thin (and thus more expensive to produce) electrodes [11–15].

Unfortunately, commercial Fe electrodes based on multi-micron-scale Fe particles only utilize 10–20% of Fe theoretical capacity and additionally suffer from slow rates and initially very low capacity, which gradually grows during the initial 20–50 “formation” cycles, thus limiting initial energy density of the cells [16]. In addition, hydrogen evolution (HE) on the Fe anode consumes electrolyte and competes with the charging reaction further reducing accessible capacity and limiting cycle life [17]. Finally, recently discussed Fe dissolution and surface passivation (formation of an insulative layer on Fe...
To address the limitations of slow initial capacity and limited rate performance of Fe anodes, the most commonly explored solution is to mix Fe or FeOx nanoparticles with conductive carbon or to make a (nano)composite of the Fe or FeOx nanoparticles and carbon (such as graphene, carbon-black, carbon nanofibers), which improves electrical conductivity of the electrodes [19,20]. Such procedures typically involve the high energy ball milling [21] or high temperature and high pressure hydrothermal methods [22,23]. These methods offer limited control of (nano)composite microstructure and suffer from the lack of composite uniformity. In addition, high surface area of the produced electrodes (and thus higher surface available for undesired hydrogen evolution reaction (HER)) and the recently observed Fe dissolution and re-precipitation to form larger agglomerates (particularly upon Fe use in a broader potential range [21]) limited success of these approaches.

Here, we report on a novel synthesis route and a novel architecture of the nanocomposite Fe-based anodes, where the crystalline FeOx nanoparticles are very uniformly distributed within nanoporous carbon spheres. This novel Fe anode architecture offers several unique advantages: i) porous carbon can control the size of FeOx nanocrystals, ii) carbon pore walls enable rapid electron transport to electrochemical reaction sites within FeOx, iii) confinement of FeOx nanoparticles prevents their agglomeration within the composite during cycling, iv) the small size of carbon pore reduces FeOx dissolution and HER. We also report for the first time a successful application of indium (In) - based organic additives, which have been infiltrated into the porous electrode particles prior to cycling. Based on the Trassatti’s volcano plot for HER [24], we hypothesized that introduced In may slow down HER (In overpotential for HER is higher than that of Fe) and prevent undesired formation of a passive surface layer (somewhat similar to the benefits of alloying aluminum (Al) with In, which helps to break down the passive hydroxide layer (Al(OH)₃) in Al-air batteries [25]).

2. Experimental section

2.1. Synthesis

FeOx/activated carbon (AC) nanocomposite was synthesized by a vacuum impregnation technique (Fig. 1). In a typical procedure, 300 mg iron pentacarbonyl (Fe(CO)₅, Sigma-Aldrich) was added drop-wise to 100 mg spherical nanoporous AC (synthesis according to the method reported by our group [26]), vacuum was applied during the interval of every second addition to ensure the effective impregnation of the precursor in the carbon matrix. The precursor-loaded composite was then preheated in Ar at 60 °C for 30 min aiming to evaporate the Fe(CO)₅ on the surface of AC, then heated up to 140 °C for another 1 h aiming to decompose the liquid Fe(CO)₅ to particle (not Fe, maybe Fe(CO)₅(x < 5)). Repeat above process for 4 times to increase the mass loading of FeOx up to 60% in AC. Then put the samples in the air to pre-oxidize the Fe(CO)₅ to amorphous FeOₓ, then annealing the samples at 300 °C to obtain crystal FeOₓ/AC.

2.2. Materials characterization

Scanning electron microscopy (SEM) micrographs have been collected on a field-emission LEO 1530 microscope (Zeiss, Germany) at a beam voltage of 5 kV and a working distance 3 mm for imaging and 8.5 mm for energy dispersive spectroscopy (EDS) studies. High resolution transmission electron microscopy (HR-TEM) with EDS line scans was performed on TecnaIG2F30 (FEI, Netherlands) operating at 100 kV. The powder X-ray diffraction (X’ Pert PRO Alpha-1, USA) using Cu-Kα radiation was employed to identify the crystalline phase of the FeOx/AC nanocomposites. The Brunauer-Emmett-Teller (BET) surface area and pore size distribution by the Density Functional Theory (DFT) method of the AC before and after loading of FeOx were characterized with an ASAP 2020 (Micromeritics Inc., USA). Electrochemical impedance spectroscopy (EIS) tests were carried out on a Gamry Reference 600 Potentiostat/Galvanostat/ZRA (Gamry Instruments, Inc., USA) with amplitude of 10 mV over the frequency range from 100 kHz to 0.05 Hz.

2.3. Electrochemical characterization

The anode electrode paste film was prepared by mixing 70 wt% of FeOx/AC nanocomposites, 10 wt% of polytetrafluoroethylene, PTFE (Sigma-Aldrich, 60 wt% suspension), 10 wt% of Bi₂O₃ (99.8%, Sigma-Aldrich), 5 wt% FeS (99.9%, Sigma-Aldrich) in H₂O solution of 1 wt% single wall carbon nanotubes, SWCNTs (75%, TUBALL, OCSIAL) and 4 wt% Polyvinylpyrrolidone, PVP (MW = 1,300,000, Alfa-Aesar) to form slurry. The slurry was stirred uniformly and then heated in the oven to evaporate all of H₂O. Adding some ethanol into above material and press them to form a plasticine-like materials. The produced composite was rolled to ~ 0.25 mm film and dried at 80 °C under vacuum overnight. The electrode film was cut into round piece (diameter = 1/2, 1/4″, mass loading of FeOx was ~ 5 mg cm⁻²) and pressed on to Ti mesh (Dextmet Corporation, USA) which was used as a current collector. The anodes with Na₂S or indium(III) acetylacetonate (In(acac)₃) as additives were made by dropping their ethanol solution on the FeOx/AC electrode film and then vacuum it aiming to pregnant the salts into the pores of FeOx/AC coating the particles of FeOx. The “commercial-like” anodes were made with mixture of AC and Fe particles (50-100 nm, Sigma-Aldrich) as active material using the same methods. The cathode electrode was prepared by mixing 80 wt% Ni (OH)₂ (Sigma-Aldrich), 10 wt% purified exfoliated graphite, PEG (Superior Graphite), 10 wt% PTFE in ethanol to make slurry. Other processes were the same as used in making the anodes except using a Ni foam as current collectors (the diameter of electrode film was 3/53/ 5″,mass loading of Ni(OH)₂ was ~ 28 mg cm⁻²). Sandwich-type electrochemical cells were set up in a plastic beaker with anode and cathode separated by 2 layers of porous polypropylene membrane Celgard 3401 (Celgard), and 7 M KOH + 1 M LiOH aqueous solutions were used as electrolytes. The charge/discharge tests were carried out using a multi-channel charge-discharge battery testing system (Arbin Instruments BT2000). The current densities of 150 mA g⁻¹ for charge and 200 mA g⁻¹ for discharge were selected. In all electrochemical measurements, fresh electrodes without any pre-cycling were used. Notably, we used the voltage holding at 1.73 V for 13 min at the charge step which can avoid generating excessive HE, while allowing a nearly full reduction of Fe(OH)₂ to Fe.
studies further confirm uniform infiltration. SEM studies of both the empty AC spheres and the produced FeOx/AC composite show very smooth particle surface (compare Fig. 3a and b) and the absence of FeOx nanoparticles on the outer surface of the FeOx/AC spheres (Fig. 3b), indicating high effectiveness of the impregnation procedure (Fig. 1). The ratio of FeOx in AC was \( \sim 60 \text{ wt} \% \) according to the EDS (Fig. S1), which was consistent with the TGA result. Fig. 3c–d compare the TEM micrographs of an empty carbon sphere and produced nanocomposite particle further suggesting very uniform distribution of FeOx (~5 nm, Fig. S2) within individual spheres. Fig. 3e shows the so-called Z-contrast image of produced FeOx/AC collected in the scanning transmission electron microscopy (STEM) mode of TEM. In a Z-contrast image (Z refers to the atomic number), the signal is proportional to the number electrons per unit-illuminated area of a sample, which is strongly influenced by Fe (Z = 26) and O (Z = 8) atoms. Therefore, the uniformity of FeOx within carbon can be directly visualized as a near perfect projection of a uniformly-dense spherical particle. Such observations can be additionally confirmed by energy-dispersive spectroscopy (EDS) line scan analysis, which shows that both Fe and O are distributed within the AC spheres uniformly (Fig. 3e–f).

We carried out electrochemical tests of the produced FeOx/AC anode to a commercial Ni(OH)\(_2\) cathode in aqueous alkaline electrolytes. The cathode areal capacity exceeded that of the anode to make sure the overall performance was anode-limited. Mixture of Fe particles with an average size of 50–100 nm and AC (in identical proportion) was used as a reference anode material. We could not use ~3 nm or smaller Fe or FeOx nanopowder (which may be desired for revealing the impact of the nanoconfinement since our nanoconfined particles may not exceed the AC average pore size, sub-3 nm, Fig. 2c) because such a material was not commercially available. In addition, by using larger Fe nanoparticles (still significantly smaller than sintered multi-micron Fe powder used in commercial cells) in our benchmark electrodes we could achieve reasonable electrical conductivity of the electrode in the discharged (oxidized) state and reduced HER [19]. Commercial cells typically utilize a relatively high cut-off voltage (e.g., > 1.35 V) to oxidize sintered Fe anodes incompletely to a mixture of Fe and Fe(OH)\(_2\), which helps in preventing electrode pulverization and Fe\(^{2+}\) dissolution into electrolyte and in keeping sintered particles electrically connected and electrochemically reversible. As a result, commercial cells allow thousands of stable cycles at the expense of relatively small capacity utilization (typically, \( \sim 100 \text{ mAh g}^{-1} \)). In contrast, we were particularly interested in a low cut-off voltage testing (1.0 V in full cells) because over 2× higher cell-level energy density may be attained in this case [21]. Such a low cut-off voltage should lead to Fe anode oxidizing to FeOx during cell discharge [19].

In contrast to commercial electrodes which typically exhibit extremely small capacity (e.g., 5–10 mAh g\(^{-1}\)) in the first cycle, our composite FeOx/AC electrode showed first cycle capacity of \( \sim 570 \text{ mAh g}^{-1} \) (Fig. 4a). The discharge curves showed expected two main plateaus, which are attributed to formation of Fe(OH)\(_2\) and FeO\(_4\), respectively (Fig. S3a) [18]. Unfortunately, within 50 cycles the electrode loose ~30% of the initial capacity and another ~10% in 50–100 cycles. The benchmark electrode sample consisted of larger nanoparticles mixed with AC showed modest initial capacity of 200 mAh g\(^{-1}\), but within 100 cycles its capacity approached that of the FeOx/AC (Fig. 4a). The corresponding Coulombic efficiency of FeOx/AC-based cell and commercial Fe + AC-based cell were shown in Fig. S5a-b. The discharge-charge profiles of both electrodes also looked similar, while the benchmark electrode showed higher polarization than as-produced FeOx/AC electrode (Fig. S5a,b, Fig. S4a-b). The large size of commercial Fe particles and limited conductivity of the produced electrode lead to a relatively higher polarization during initial cycles, which is consistent with its low capacity. Clearly, despite promising initial performance, the overall stability of the nanoconfined FeOx was somewhat underwhelming. However, by increasing the cut-off voltage from 1.0 V to 1.3 V the stability of the FeOx/AC nanocomposite was...
noticeably improved - capacity retention in excess of 85% was main-
tained after 200 charge-discharge cycles (Fig. 4b), although at the ex-
pense of smaller electrode capacity of ~270 mAh g$^{-1}$. Our FeOx/AC/
Ni(OH)$_2$ full cell showed an energy density of 62 Wh kg$^{-1}$ at a power
density of 26 W kg$^{-1}$, which is higher than that of reported aqueous Li-
ion batteries and Na-ion batteries (Fig. S6, Table S1).

Encouraged by promising 1st cycle performance of the FeOx nano-
particles confined in carbon nanopores, we became interested to in-
vestigate the impact of two types of electrode additives pre-infiltrated
into the nanocomposite pores – (i) Na$_2$S and (ii) In(acac)$_3$. We had
hoped that the presence of such additives may enhance accessible cell
energy and stability.

Testing of the Na$_2$S additive was motivated by the previously ob-
served positive impact of FeS, PbS and Bi$_2$S$_3$ [28,29]. It was proposed
that the sulfides greatly suppresses Fe electrode passivation and in-
creases the discharge capacity especially at high rate [30,31]. We hy-
pothesized that distribution of Na$_2$S directly on the surface of active
material of electrodes may similarly increase the electronic conduc-
tivity of the Fe electrodes by S$^2-$ adsorption on the electrode/elec-
trolyte interface but also provide improvement in the ionic conductivity
of the passive film because Na$^+$ may be incorporated in the passive
layer. The estimated fraction of infiltrated Na$_2$S salt was 5 wt%.

Fig. 3. SEM and TEM images of as-synthesized empty AC and FeOx/AC: (a, c) empty AC; (b, d) FeOx/AC; STEM image (e) and EDS line scan result (f) of FeOx/AC nanocomposite, showing uniform distribution of FeOx within a AC sphere.
Unfortunately, the overall improvement (if any) was rather marginal (Fig. 4c). The discharge capacity was reduced by ~20%, presumably due to small increase in the electrode mass after Na$_2$Si infiltration and potentially blocking (by adsorbed Na$_2$S) of some of the electrolyte from reaching active material. Possible ethanol residues (from Na$_2$S solution infiltration) should unlikely affect cell performance since these should readily dissolve into aqueous electrolyte. On a positive side, we noticed increased discharge voltage plateaus of Na$_2$S-containing electrode (Fig. 4d, Fig. S4c), suggesting the positive impact of Na$_2$S in lowering electrode polarization. Based on previously published improvements in using sulfi de-based additives [32–34], we hypothesized that Na$_2$S enhanced the Fe anode activity by modifying its surface chemistry, for example by forming NaFeS$_2$ which should increase both electronic and ionic conductivity of the Fe electrode and prevent rapid passivation [35,36]. The corresponding Coulombic efficiency of FeO$_x$/AC+Na$_2$S-based cell was shown in Fig. S5c.

The second, arguably significantly more innovative, additive we applied and tested was In-based organic compound, In(acac)$_3$. We had two hypotheses to believe that such an additive may provide various performance enhancements. Firstly, formation of In-comprising layer on the electrode surface (at the electrode-electrolyte interface) should slow down HER due to significantly higher overpotential for H$_2$ evolution on In than on Fe surface [23]. Secondly, analogous to bismuth additives [37], we expected that In may prevent undesired formation of a passive surface layer on the active material, as previously observed in metal-air batteries [38].

Electrochemical studies of the In(acac)$_3$ containing electrode showed multiple unexpected outcomes (Fig. 4e-f, Fig. S4d). First, the 1st cycle capacity of the electrode was remarkably high (~700 mAh g$^{-1}$). Clearly, the capacity utilization was enhanced significantly. Because In(acac)$_3$ exhibits very low solubility in aqueous solutions, it was expected to at least partially block some of the pores. However, it evidently did not prevent access of electrolyte to active material. Due to relatively high reduction potential for In/In$^{3+}$ ($-0.335$ V vs. Ag/AgCl) [39], formation of In-comprising surface layer on the Fe surface is expected. As previously discussed, such a layer may enhance electrochemical activity of the Fe anodes. The second observation was that the higher voltage plateau (~1.37 V) increased by over 2×, while the low voltage plateau (~1.15 V) almost completely disappeared. This is, of course, highly advantageous for practical applications because it increases average cell potential and simplifies battery electronics. Such an unusual electrochemical behavior may suggest a direct oxidation of Fe to Fe$_3$O$_4$ without an intermediate phase of Fe(OH)$_2$. Because this phenomenon was also observed in cells with In$_2$O$_3$ as additive (Fig. S3c), we propose that In or In-comprising ions act as catalyst(s) for oxidation of Fe. Because oxidation from Fe to Fe$_3$O$_4$ is accompanied by the largest volume changes (of 372%), avoiding this phase formation reduces internal stresses. In addition, because physical constrains to the needed volume changes may reduce capacity utilization [16], avoiding Fe(OH)$_2$ phase formation may
potentially contribute to higher capacity achieved (Fig. 4f). The third observation was excellent capacity retention for the first ~5 cycles (compared to pure FeOx/AC electrode or the electrode with Na2S additives). As will be later discussed, capacity decay in our electrodes correlates with active material dissolution and re-precipitation. It is conceivable that electro-deposited In surface layer may have reduced the dissolution of Fe. At the same time, during charging In should at least oxidize (e.g., forming InO2) and partially dissolve in electrolyte until the concentration of InO2 eventually reaches saturation in the electrolyte. Based on prior studies on Ni/Zn cell where In doping into the metal anode was observed and provided multiple benefits (e.g., improving electrical contact with the current collector, enhancing electrode stability, reducing side reactions with electrolyte and improving kinetics) [40,41] and based on the ~0.28 at% solubility of In in Fe at room temperature [42], we expect that some portion of In may also be incorporated in the surface layer on active material. Interestingly, in 40–70 cycles stability of cells with different electrode additives become comparable and their capacities remain within approximately ±20%, suggesting that by the 40th cycle the effectiveness of additives become diminished. Furthermore, we observed that after ~70 cycles with In(acac)3 additives started to exhibit very significant oscillations in capacity. Multiple cells exhibited similar performance and we are confident that the phenomenon was real. As will be discussed later, such cycle-to-cycle capacity variations may be related to structural changes in the electrodes and the associated blocking the active anode surface. The corresponding Coulombic efficiency of FeOx/AC + In(acac)3-based cell was shown in Fig. S5d.

EIS analyses provided complementary insights about the influence of cut-off voltage and additives on the performances of FeOx/AC electrode. The experimental Nyquist and Bode plots (here we just show the Nyquist plots, Fig. 5a–c, Fig. S7b) of full cells were fitted using the equivalent circuits, as shown in Fig. 5d and Fig. S7a. Table 1 shows the calculated values for the Ohmic (mostly electrolyte) resistance (Re), the charge transfer resistance of the anode (Ra), the charge transfer resistance of the cathode (Rc), and the electrode/electrolyte interface resistance (Ri) of the full cells. Here we discuss just the Ra and Ri contributions because the overall performance is anode-limited.

While the initial FeOx/AC-based cell showed lower Ra resistance (3.2Ω) than the initial benchmark cell based on a larger size commercial Fe nanopowder (4.2Ω), after the 100 cycles the resistance of the FeOx/AC increased and the trend reversed. More specifically, we observed higher Ra (9.5Ω for 1.0 V cut-off voltage after 100 cycles, 6.5Ω for 1.3 V cut-off voltage after 100 cycles) for the cycled FeOx/AC-based cell than that of the cycled benchmark cell (6.6Ω for 1.0 V after 100 cycles, 4.6Ω for 1.0 V after 100 cycles). The substantial increase in the Ra resistance of the FeOx/AC-based cells may indicate significant changes in the electrode morphology. This may not be extremely surprising because we previously observed dissolution and re-precipitation of Fe3O4 in the form of nanoporous, nanocrystalline powder [12]. When increasing the cut-off voltage, the Ra of the cells are reduced while the Ri remain almost the same (Fig. 5a, Table 1). This suggests faster reaction kinetics at higher cut-off voltages, which, in turn, may lead to higher capacity retention (due to higher fraction of the total charging current being consumed by electrodes compared to a side reaction), as previously observed and discussed (Fig. 4b).

Table 1
Impedance parameters derived using equivalent circuit model for Ni/Fe batteries at discharge state.

<table>
<thead>
<tr>
<th>Anodes</th>
<th>Cut-off Voltage (V)</th>
<th>Cycle number</th>
<th>Ra (Ω)</th>
<th>Rc (Ω)</th>
<th>Rr (Ω)</th>
<th>Ri (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial Fe + AC</td>
<td>–</td>
<td>0</td>
<td>0.6</td>
<td>4.2</td>
<td>0.3</td>
<td>–</td>
</tr>
<tr>
<td>FeOx/AC + Na2S</td>
<td>1.0</td>
<td>100</td>
<td>0.3</td>
<td>6.6</td>
<td>0.1</td>
<td>1.8</td>
</tr>
<tr>
<td>FeOx/AC + In(acac)3</td>
<td>1.3</td>
<td>100</td>
<td>0.5</td>
<td>4.6</td>
<td>0.2</td>
<td>1.9</td>
</tr>
<tr>
<td>FeOx/AC + In(acac)3</td>
<td>–</td>
<td>0</td>
<td>0.7</td>
<td>3.2</td>
<td>0.5</td>
<td>–</td>
</tr>
<tr>
<td>FeOx/AC + Na2S + In(acac)3</td>
<td>1.0</td>
<td>100</td>
<td>0.3</td>
<td>9.5</td>
<td>0.1</td>
<td>6.6</td>
</tr>
<tr>
<td>FeOx/AC + Na2S + In(acac)3</td>
<td>1.3</td>
<td>100</td>
<td>0.1</td>
<td>6.5</td>
<td>0.1</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Fig. 5. EIS characterization: comparison of Nyquist plots of Ni/Fe batteries made with (a) FeOx/AC and commercial Fe + AC after 100 cycles, (b) FeOx/AC, FeOx/AC + Na2S and FeOx/AC + In(acac)3 after 100 cycles, (c) FeOx/AC + In(acac)3 after different cycles, (d) Equivalent circuit used to fit the EIS.
16.1 to 14.2 Ω. This is consistent with slightly lower polarization, as discussed in a previous section (Fig. 4d). The EIS of In(acac)$_3$-comprising cells after 10, 50, 80 cycles (Fig. 5c) show a very large gradual resistance increase (to ~25.5 Ω). When compared to other cells (Fig. 5b) In(acac)$_3$-comprising cells show by far the largest resistance. This larger resistance (polarization) growth correlates well with the capacity fluctuations (Fig. 4e).

In order to gain a better understanding on the origins of above observations, post-mortem analysis of the cycled anodes (in the discharged state) was conducted. X-ray diffraction (XRD) reveals the
presence of both Fe₃O₄ and Fe in the anodes after 100th cycles (Fig. 6). The presence of Fe peaks indicates that some portions of the anode become inactive over time. The most dramatic increase in the Fe peak was observed in the cells comprising In(acac)₃ after 100 cycles when the capacity was dropped significantly (Fig. 4e). At the same time, the intensity of Fe₃O₄ and Fe peaks in the electrodes with In(acac)₃ at 10th and 50th cycle are similar with the pure FeOₓ/AC electrode, which is consistent with their capacity retention at these cycles.

Post-mortem SEM studies showed dramatic changes in the electrode morphology after cycling (Fig. 7, Fig. S8). First, we observe significant number of Fe/FeOₓ particles outside the AC spheres in all FeOₓ/AC nanocomposite samples. These are produced by Fe/FeOₓ dissolution from the inner pores of the FeOₓ/AC nanocomposites and their re-precipitation on the outer surface. While when normalized by the BET SSA (nearly 900 m² g⁻¹) the dissolution is relatively moderate, it evidently does become quite significant over time. Such irreversible dissolution-precipitation process is likely responsible for the performance degradation (capacity fade) because newly formed particles do not have direct contact with conductive additives.

Both the cut-off voltage and additives affect morphology and the degree of Fe dissolution from FeOₓ/AC electrodes significantly. For example, using 1.3 V as a cut-off voltage results in noticeably fewer FeOₓ particles formed on the outer surface of the AC spheres (compare Figs. 7a and b or c and d), in full agreement with the improved stability observed in cells cycled at higher cut-off voltage (compare Figs. 4b and 7e). The comparison of the amount of Fe on the Ni cathodes (which is expected to be proportional to the amount of the dissolved Fe) as measured by EDS also confirms this (Fig. 8). Comparing the morphologies of FeOₓ/AC nanocomposites and benchmark electrodes composed of the mix of commercial Fe nanoparticles and AC particles (cycled at both 1.0 V and 1.3 V cut-off voltage limits), we observed larger and more crystalline particles in the benchmark electrodes (compare Fig. 7a and c or Fig. 7b and d). This suggests that nanoconfinement helps to mitigate the dissolution-precipitation and is particularly impressive considering much smaller size of the nanoconfined particles (which should exhibit much faster dissolution due to their higher surface energy and higher surface area). The well-defined shape of the crystals formed in the benchmark samples (Fig. 7c and d) is likely related to their repeated dissolution-growth on the surface of the large pre-existing particles.

When comparing the effect of additives, we observe that the addition of Na₂S reduced the dissolution considerably, while the addition of In(acac)₃ didn’t impact the dissolution (compare Fig. 7e and f), the degree of which was similar to that observed in the pure FeOₓ/AC electrode. We propose that Na₂S may have enhanced heterogeneous nucleation/deposition of the re-precipitated Fe back onto the surface of the nanoconfined Fe/FeOₓ. It is also possible that the presence of Na₂S somewhat reduced the solubility of HF₆FeO₄⁻ ions into electrolyte. In contrast, the presence of In(acac)₃ and the expected electrodeposition of In onto the surface of nanoconfined Fe/FeOₓ might have triggered homogeneous nucleation and growth of new particles outside the AC spheres. The adsorption of organic tail of the salt (acetylacetonate) into

Fig. 9. TEM micrographs of cycled anodes at discharge states after cycles: FeOₓ/AC at cut-off voltage of (a,d)1.0 V, (b,e) 1.3 V; FeOₓ/AC+Na₂S (c,f) and FeOₓ/AC + In(acac)₃(g-l) at cut-off voltage of 1.0 V.
the carbon nanopores (porous carbon is well known to be an excellent separator of various organic species [43–45]) may have also contributed to reduced re-deposition of Fe within the nanopores. The spherical shape and a high number of the re-deposited nanoparticles (Fig. 7f) support the homogeneous nucleation and growth theory. The significantly agglomerated large particles formed in the samples with In(acac)3 (Fig. 7f) reduced the outer surface area greatly. As a result, In-electro-deposited on their surface might have blocked electrochemical activity of Fe, leading to dramatic cycle-to-cycle capacity oscillation (after ~70 cycles in Fig. 4e).

Post-mortem TEM studies showed that the majority of re-precipitated particles in products of all the cycled and discharged (oxidized) electrodes are Fe3O4 (Fig. 9). This agrees with the XRD results (Fig. 6). Many Fe3O4 particles formed in the cells cycled with 1.0 V as a cut-off voltage (Fig. 9a,d) are porous. In contrast, Fe3O4 particles found in the cells cycled with 1.3 V cut-off voltage were crystalline and dense (non-porous) (Fig. 9b,e). When comparing the impact of additives, In(acac)3 resulted in a significantly more porous Fe3O4 formation after cycling than that of Na2S-comprising electrodes. Higher surface area and more porous Fe3O4 are expected to result in higher electrochemical activity. As such, the observed results are consistent with electrochemical performance (Fig. 4). Fig. 10 illustrates the simplified schematic of the cycling process of commercial-like electrode and FeOx/AC based electrode according to the discussion above.

4. Conclusions

In summary, we report on a simple method to produce nanostructured composite Fe-based anode powder, where FeOx nanoparticles are uniformly distributed within nanopores of activated carbon. The Ni/Fe battery based on FeOx/AC nanoparticle composite demonstrate a remarkably high first cycle discharge capacity of up to 600 mAh g⁻¹. As expected, electrochemical cycling induced dissolution and re-precipitation of the Fe/FeOx outside the particle surface. However, nanoc confinement and increased discharge cut-off voltage suppressed the Fe dissolution substantially and improved discharge capacity retention to 85% capacity after 200 cycles. Two additives Na2S and In(acac)3 affected cell performance noticeably. Na2S reduced electrochemical polarization and dissolution, while reducing accessible capacity. In(acac)3, in contrast, increased accessible capacity and changed the discharge profile markedly - instead of two we obtained a single high voltage discharge plateau, which increases accessible energy density from Fe-based anodes and is highly advantageous for battery management system because a near-constant voltage is maintained over the whole discharge. The reported new opportunities in the century-old chemistry show great promises for safer and lower cost aqueous batteries from low-cost earth abundant Fe.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2018.03.035.

References

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