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In this work, we have studied a 2% copper substituted core shell type iron/iron carbide as a negative electrode for application in energy storage. The NanoFe-Fe3C-Cu delivered 367 mAh g−1 at ≈80% current efficiency, successfully running for over 300 cycles. The superior electrode kinetics and performance were assessed by rate capability, galvanostatic, potentiodynamic polarization measurements in 6 M KOH electrolyte and at ambient temperature. Ex-situ XRD characterizations and SEM images of both the fresh and used electrode surfaces show that nanoparticles were found to be still intact with negligible particle agglomeration. The electrodes have shown stable performances with low capacity decay, whereas sulfur dissolution from the additive Bi2S3 was found to decrease the charging efficiency with time. This core-shell type structured nano material is, consequently, an auspicious anode candidate in alkaline-metal/air and Ni-Fe battery systems.

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Electricity generation away from fossil fuels by renewable energy resources (RER) is increasing at a remarkable pace both as a means of mitigating greenhouse gas emissions as well as offsetting the global energy demand for sustainable development. Since the end of the 1990s, the world cumulative energy generation by both wind and solar has shown an exponential growth rate. In 2015, the global installed capacity of photovoltaics was 227.1 GW an increase by 25% and the total installed wind power was 432.9 GW, a rise by 17% compared to 2014 for both energy systems.1,2 However, both wind and solar are very dependent on weather conditions and there is a high quest for electrical energy storage (EES) for integration with these renewables. The variability in energy output is due to the stochastic nature and availability of the renewable sources, unreliable demand and supply of electricity, distributed energy generation, maintenance and utilization of load balance in peak shaving and leveling, stabilization of transmission and distribution to the grid, uninterruptable power supply with frequency control, voltage fluctuations and energy arbitrage. EES is considered to be vital and indispensable technology for both utility and transport applications.1,3–5 Among EES technologies, electrochemical energy storage systems in the form of batteries have characteristic features in the form of modularity and scalability, fast response time and high energy efficiency, although they do significantly differ in energy and power densities, charge and discharge duration, cycling behavior and capital cost.

There are several rechargeable (secondary) battery energy storage systems (BESS) that are widely used or are under development phases and these among others include: lead-acid, Li-ion, the nickel-based batteries (Ni-MH, Ni-Cd, Ni-Fe, Ni-Zn, NaNiCl2), redox flow batteries (Vanadium, Zn-Br, Zn-Cl, Zn-Ce, Fe-Cr, V-Br), NaS and Air-metal batteries (Fe-air, Zn-air, Li-air, Mg-air).6–10 The last type of “batteries” are essentially a hybridization of anodes in the form of metals and a fuel cell, which is supplied by abundant air/oxygen to be reduced at the cathode without the need for storage. Even though Li is costly due to limited mine production that is currently estimated at 13.5 × 106 tons of known reserves11 Li ion has become the default battery as the most advanced system in terms of high energy density, high power density, high efficiency and increased cycle life to power portable electronic devices as well as hybrid and electric vehicles. Thus, the use of hybrid, plug-in or all-electric vehicles and eventual EES with the increasing interest in renewable energy is going to cause a huge strain on Li price showing that it will not be a cost effective solution.12–14 In this aspect, utilization of metal air systems, such as Fe-air, Zn-air, Mg-air and Al-air are deemed cheaper for grid level energy storage. Each system has its own merits and demerits. Though Al, Mg, Zn systems have higher theoretical energy density, they have inherent problems like dendrite formation, uneven metal deposition, corrosion of metal anode, reactivity/dissolution and they are more costly than the Fe-based systems. Furthermore, the world resources and known reserves of iron is 230 × 109 tons making it as the most available, least expensive and non-toxic to be used for large scale BESS.15,16 The use of alkaline electrolyte offers higher ionic conductivity, corrosion resistance and better safety issues compared to organic or acidic electrolyte system.

Iron-air and Ni-Fe secondary batteries are one of the systems, in view of their early application in traction systems with an energy density of 80 Wh kg−1 and 2000 cycles.6,17 The electrode reaction products are insoluble in alkaline media, which makes this system to show stable performances. The US DOE has set up long-term targets for the realization of storage technology for the grid with cost and performance based on capital cost of $150/kWh, system efficiency of 80% and cycle life of 5000.18 Narayanan et al.19 have shown that the Fe-air battery has the potential to meet the above goals by considering the major advantages and disadvantages of various battery systems. However, this battery has the limitations associated with the iron electrode having low charge efficiency due to the concurrent hydrogen evolution reaction during charge, underutilization of the active material as well as resistive discharge product that increases the overpotential for charging, which in turn deteriorate the rate capability.19,20

To overcome the hydrogen evolution reaction, various sulfide and carbon additives have been used as electrode or electrolyte additives. Among them, few are considered as effective: Bi2S3, Bi2O3+FeS, K2S, Na2S, organo-sulfurs.19,21–23 Most of the compounds form different iron sulfide phases, while elemental bismuth metal is formed during charging increasing the overpotential for hydrogen evolution.24 Other major problems like low active material utilization and passivation induced capacity decay may take place. To subdue these problems, nano iron materials and nano-carbon composites have been used;25–28 albeit particle agglomeration and increased hydrogen evolution were found to be the primary causes of failure to achieve several charge/discharge cycles.24,25,30 C-Y Kao et al.31 have recently reported a nano iron/copper composite material with high concentration of Cu displaying a high rate discharge capacity of 800 mAh g−1 and at a mass activity of 3200 mAh g−1. In our present work, we use core-shell type nano iron/carbonate/copper (NanoFe-Fe3C-Cu) composite as anode material to be used in iron batteries. The rationale behind this is that iron
carbide shell could protect iron core against particle agglomeration, where the outer shell serves as a shield against swelling/passivation and the 2 wt% copper maintains electronic conductivity and stability. Electrode material based on this combination showed stable performances for 150 cycles with a capacity 370–300 mAh g⁻¹ at 100 mA g⁻¹. Negligible morphological changes were seen in the electrode structure. Various characterization tools were used to elucidate the factors affecting the charge/discharge characteristics of the electrode composite.

Experimental

The active material copper-doped nano iron carbon composite (NanoFe-Fe₃C-Cu) was supplied by Höganas AB. The composition based on DTA (differential thermal analysis) and elemental analysis was 2 wt% Cu and 10 wt% carbon with remaining 88 wt% as iron. The BET surface area was found to be 7 m² g⁻¹.

The powder sample as well as the charged and discharged electrodes were characterized by X-ray diffraction (XRD) using Siemens Bruker D5000, equipped with Ni filtered Cu Kα source (30 mA, 40 kV). Phase identification was done in EVA software and the plane reflection were indexed using powder diffraction file (PDF ). The morphologies of the fresh samples of the nanoFe-Fe₃C-Cu along with formation and charged/discharged electrodes, were taken by Zeiss Ultra-55 Scanning Electron Microscope (SEM), while transmission electron micrographs (TEM) were obtained by JEOL JEM-2100F.

The electrode was prepared by mixing the following compositions according to the mass ratio: NanoFe-Fe₃C-Cu (85%), Ketjenblack–EC-3001 (5%), Bi₂S₃ (5%) and PTFE 5% (60 wt% in water dispersion). Wet paste was prepared by adding a hydrocarbon solvent (Shellsol D-70) to make the electrode composite. This wet mass was rolled on a nickel wire screen having 100 mesh size. The electrode was pressed at 375 kg cm⁻² and finally sintered at 325°C for 30 minutes in a N₂ atmosphere. The final electrode thickness and active material loading were 0.35 mm and 32 mg cm⁻², respectively.

Electrochemical measurements were conducted in 6 M KOH electrolyte in a three-electrode set-up having the NanoFe-Fe₃C-Cu as the working electrode, Ni wire mesh as the counter electrode and Hg/HgO as the reference electrode. In order to achieve stable performances, the electrodes were treated for 30–40 cycles at C/7 and C/10 rates. Thus, after being nominally “formed”, the electrodes were charged at 50 mAg⁻¹ and discharged at 100 mA g⁻¹ whereas the discharge cutoff voltage was kept at −0.8 V vs Hg/HgO. In the rate capability tests, the discharge current was varied from 50 to 900 mA g⁻¹ which would be related to the theoretical capacity of iron of 962 mAh g⁻¹. All the reported capacities are based on the mass of total iron in the composite. Cyclic voltammetry was conducted on a fresh electrode at a sweep rate of 1 mVs⁻¹ and within a potential window of −1.35 to −0.4 V. Potentiodynamic polarization curve was obtained in the anodic direction up to −0.75 V at 0.167 mV s⁻¹ scan rate. In the galvanostatic polarization, current was varied from 1 mA cm⁻² to 15 mA cm⁻². In each step, a constant current was maintained for 5 minutes and the data was corrected for the effects of mass transfer and ohmic resistance. Corrections for ohmic resistances were done by the current interrupt method integrated in the instrument, while by plotting the potential response to the square root of time and by extrapolating at t = 0 was used for mass transfer correction.

Electrochemical impedance spectra were measured for fully charged electrodes in the 100 mHz to 100 kHz range with 5 mV AC amplitude at an open circuit potential.

The electrochemical studies such as the cycling behavior and rate capability were performed and the data acquired on Land battery testing system (CT 2001–5 V 2A BTS System). Cyclic voltammetry, potentiodynamic- and galvanostatic polarizations were conducted by SP-50 potentiostat (Biologic Science Instruments) and the impedance measurement was obtained by Gamry PCI 4 G750 potentiostat. Impedance analysis was performed on Biologic science instrument with a software (EC-Lab 10.44).

Results and Discussion

Material characterizations.—Fig. 1 shows the XRD pattern of the NanoFe-Fe₃C-Cu, comprising of the α-iron, iron carbide and copper. The different crystal planes in the pattern are identified using the powder diffraction file directory (PDF numbers). The PDFs for α-iron, iron carbide (cementite and coherentite) and copper are 00-001-1267, 00-003-1056, 01-075-910 and 00-001-1241, respectively. Based on the intensity ratio, the α-iron is the major phase, the remaining iron carbide and copper being less pronounced. No carbon diffractions were detected between 25 and 30° 2θ angles. The (211) plane dominates in the 20 region between 44.5 and 45.4°35,36 and the crystallite size is about 52 nm according to calculations by the Scherrer equation.

Fig. 2. (a–e) show the transmission electron microscopy (TEM) and selected area electron diffraction (SAED) analysis of the nano iron sample. It is evident from Figs. 2a–2b that the particles are in a core-shell structure with particle sizes in a typical range of 20 to 100 nm, where one to four particles may also be encapsulated into one bigger particle. Higher magnification of the particles show shell thickness to be 20 nm or less as shown in Fig. 2c. The SAED pattern in the inset Fig. 2c differentiates the phases of the core-shell. The inter-planar distances obtained from the first diffraction spot gives 1.04 Å for core and 1.82 Å for shell, corresponding to (220) plane of α-iron and (122) plane of Fe₃C (coherentite) phase, respectively. To fit the exact phases in the shell material’s electron diffraction, interplanar distance were measured at concentric diffraction spot marked in Fig. 2d as “a,b,c,d”, where respective diffraction plane was marked in the inset table. These results show that the shell is made-up of Fe₃C coherentite phase37 with corresponding 10 lattice fringes with an interplanar distance of 35.82 Å (Fig. 2e), which is closer to the value of Fe₃C coherentite phase at the 002- plane (Fig. 2d). This carbide layer is expected to protect the nano particle growth and agglomeration. Thus, the TEM-SAED result corroborates the XRD findings in Fig. 2, where the nano powder consists of α-iron and Fe₃C coherentite. The presence of copper was not possible to detect in the TEM to identify, probably due to its low concentration (2 wt%), high dispersion and/or interference by the larger core-shell particles.

Electrochemical characterizations.—The cyclic voltammograms of the first, second, third and tenth cycles, are shown in Fig. 3. In the initial three cycles, there is a broad peak (−0.9 V to −0.7 V) with two shoulders at −0.825 V and −0.76 V, which are assigned to be related to (Eqs. 2 and 5), i.e. generation of reduced sulfide ions during charge (Eq. 4) and further recombination of these ions with iron hydroxide to form iron sulfide within the electrode structure.38–40 The amount of iron sulfide formation is proportional to the availability of iron (II) hydroxide formed during the forward reaction. After ten test cycles, there are three well-developed oxidation peaks (Aₛ observed at −0.966 V, A₁ at −0.70 V and A₂ at −0.44 V), which are related to the adsorption of hydroxide ion,41 further oxidation of Fe to Fe(II) and Fe(II) to
Fe(III) respectively. The reaction schemes are as follows:

\[
\text{Fe} + 2\text{OH}^- \leftrightarrow [\text{Fe(OH)}_{\text{ads}}] \quad [1]
\]

\[
\text{Fe} + 2\text{OH}^- \leftrightarrow \text{Fe(OH)}_2 + 2e^- \quad E^0 = -0.975 \text{ V vs. Hg/HgO} \quad [2]
\]

\[
3\text{Fe(OH)}_2 + 2\text{OH}^- \leftrightarrow \text{Fe}_3\text{O}_4 \cdot 4\text{H}_2\text{O} + 2e^- \quad E^0 = -0.756 \text{ V vs. Hg/HgO} \quad [3]
\]

\[
\text{Bi}_2\text{S}_3 + 6e^- \leftrightarrow 2\text{Bi} + 3\text{S}^{2-} \quad E^0 = -0.918 \text{ V vs. Hg/HgO} \quad [4]
\]

\[
\text{S}^{2-} + \text{Fe(OH)}_2 \leftrightarrow \text{FeS} + 2\text{OH}^- \quad [5]
\]

The first peak (A0) has in recent studies been assigned to hydrogen oxidation and hydroxyl ion adsorption. Its appearance varies for different electrode materials as for example −0.87 V in FeS/graphene composite, −0.93 V in FeS/carbon electrode materials or −0.95 V in Fe/C composite electrode. This phenomenon of the removal of adsorbed hydrogen from the electrode during the anodic sweeping has also been observed by the electrochemical quartz crystal microbalance method, confirming the initial (Eq. 1) reaction step. It was reported that the oxidations of iron carbide and copper (to Cu2O) take place at −0.49 V and −0.4641 V vs Hg/HgO, respectively. In our case, the oxidation of copper may also exist in parallel with the Fe(II)/Fe(III), though its peak was not distinct due its relatively small amount in the electrode composite. However, the oxidation of iron carbide at its oxidation potential is not visible compared to the iron redox couple. Ujimine et al. reported that high concentration of Fe3C as electrode material is oxidized irreversibly to Fe3O4 with its consumption and disappearance after only five cycles. In our further study of the charge/discharge cycling for capacity testing, the copper and iron carbide do not interfere as their oxidations take place outside the potential range of operation (−1.2 to −0.75 V vs Hg/HgO). In the reduction direction, the peak C1 at −0.55 V, corresponding to FeOOH peak, faded after two cycles. Similar observations were reported by Shangguan et al. of the redox couple of Fe(OH)2/FeOOH as may be related to an intermediate activation process of the electrode. The clear and broad peak (C2) observed at −1.12 V corresponds to the reduction of Fe (II) to Fe(0), and is shifted toward more negative potentials with increasing cycle number after initial activation of the electrode. Following this peak, however, the hydrogen evolution becomes predominant at potentials more negative than −1.21 V. No clear peaks on the reduction of Fe3O4 to Fe(OH)2 can be observed in the voltammogram, as this reaction would have preceded directly the Fe(OH)2/Fe-peak starting at −0.9 V, causing a broadening of the peaks. The mix potentials of Fe (III) to Fe(II) and to Fe(0) of the copper doped NanoFe-Fe3C-Cu gives remarkably high current (0.5 A) at the peak potential of −1.12 V, which is beneficial for battery operations and utilization at high discharge rates.
Potentiodynamic polarization experiment was used to examine the passivation characteristics of NanoFe-Fe3C-Cu. Passivation is the phenomena when the current is limited by the oxidation of iron and the buildup of hydroxide layer and a sulfur containing electrode or electrolyte system tends to prevent the current limiting passivation. The anodic polarization curve is shown in Fig. 4a. When the electrode is polarized toward $-0.75$ V vs. Hg/HgO, the current started increasing steeply from $-0.98$ V to $-0.95$ V (slope 0.9 mV·mA$^{-1}$), then increased linearly from $-0.95$ to $-0.75$ V (slope 0.2 mV·mA$^{-1}$). These two different slope values suggest that different reaction mechanisms were taking place. The first part until $-0.95$ V could be related to the adsorption of the hydroxyl ion as also observed by the cyclic voltammetry in Fig. 3 (peak A$_0$). The latter value was the active iron to iron hydroxide (Fe/Fe$^{2+}$) formation. A current limiting passivation does not appear during the anodic polarization, where maximum current density of 40 mA cm$^{-2}$ at $-0.75$ V was achieved. Thus, the electrode has the propensity to withstand high discharge currents without passivation. The main possible factors for this high discharge current, in addition to the structure of the nanomaterial with Fe$_3$C, is the admixture or presence of both bismuth sulfide and copper improving the overall performance characteristics and conductivities of the electrode.31,41

Fig. 4b shows the galvanostatic polarization curve of the NanoFe-Fe$_3$C-Cu electrode. The data was collected in the anodic direction. This polarization at low currents provides two important kinetic parameter values: the Tafel slope (b) 35 mV·dec$^{-1}$ and the exchange current density ($i_0$) $-0.26$ mA cm$^{-2}$. The high value for the exchange current density, which shows the relative rate at the equilibrium condition with its reversibility in the anodic/cathodic direction, is to a large extent caused by the nanomaterials used. The Tafel slope compared to the literature data was either lower, as for the case of iron powder with different metal sulfide (40–80 mV decade$^{-1}$) and sulfide modified iron electrode (63–72 mV decade$^{-1}$), or on par with carbon grafted active material (30–32 mV decade$^{-1}$). The Tafel slope is close to the value 3RT/2F assuming that the potential dependence of the coverage of the intermediate species is equal to 1. These parameters would mean that the iron, iron carbide shell and the copper doping most probably do accelerate the electrode kinetics, with the transfer of electrons at the electrode/electrolyte phase boundaries, enhancing higher currents at lower overpotentials and accordingly contributing to higher discharge rates.

Fig. 5a shows the charge/discharge profiles from the first to the 300th cycles. In the first cycle, charging and discharging plateaus stay at $-1.125$ V and $-0.95$ V vs. Hg/HgO, respectively. After 300 cycles, the charge potential increased stepwise from around $-1.12$ V to $-1.22$ V showing increased hydrogen evolution with time. Moreover, the discharge plateaus moved to $-0.90$ V from the initial $-0.93$ V. The shifts of this plateau suggest that the overpotential for the Fe/Fe(OH)$_2$ redox process keeps increasing. This is in agreement with the pore plugging model, where the inner pores of porous electrodes are plugged by the discharge products leading to higher ohmic drops.46 During the charge and discharge cycles, however, the specific capacity shows an increase from the first to the 50th and then 100th cycles and thereafter.
consequentially decaying to lower values. Fig. 5b shows the discharge capacity as a function of cycle numbers. During the initial 100 cycles the electrode delivered 350 mAh g$^{-1}$ of capacity with 80% of charge efficiency. After 300 cycles, the capacity gradually decreased to 250 mAh g$^{-1}$ with 55% charge efficiency. The main causes for the decrease in charge efficiency and capacity may be ascribed to the disappearance of sulfur from the iron electrode, where increased electrode resistance might ensue. This has been found to be the usual trend observed in bismuth sulfide containing electrodes where sulfur is found in an oxidized state in the counter electrode after extensive cycling.3,8

In order to investigate how the electrochemical frequency response changes with the cycling behavior of the electrode, electrochemical impedance analysis was carried out at open circuit potential (−0.95 V) as complementary to the above measurements and the results are shown in the Nyquist plot in Fig. 6. Experimental Nyquist plot was fitted with the model circuit shown in the inset in Fig. 6, there is a clear deviation from the ideal behavior of impedance not purely being capacitive due to the frequency dispersion and which would be explained by a constant phase element (CPE). This is specially the case with porous electrodes having surface inhomogeneities and geometries, characterized through pore size, distribution and shape, electrode thickness and interspacing.49–51 Table I shows that the fresh electrode displays higher charge transfer resistance, ohmic resistance and lower double layer capacitance, which might be ascribed to the higher hydrophobicity and low porosity of the electrode/electrolyte interphase. The PTFE and initial structure of the carbon black hinders the wettability and intrusion of the electrolyte to the electrode and thereby increase the hydrophobicity. After formation, the electrode resistances ($R_s$, $R_{ct}$) decrease substantially by factors of 2.3 and 17, respectively. As the double layer capacitance is directly proportional to the surface area and surface coverage of sulfur ions, its value increases from fresh electrode to formed electrode implying increased accessibility of the surface for the electrode reactions and the sulfur species.21 Therefore, formation or activation might prompt changes in the electrode texture, bulk conductivity and porosity. After 200 cycles the ohmic resistance and charge transfer values increased significantly from the values at 35 cycles, entailing the resistive component (uncharged passive iron hydroxide, sulfur depletion) and buildup in the electrode/electrolyte interphase. Moreover, the double layer capacitance maintains high value due to the presence and formation of oxide forms of iron and an increase in the surface roughness (see Table I). The double layer capacitance of iron in alkaline media is around 150 μF cm$^{-2}$48 In our study, we found the values to be more than 300 to 800 times higher than the above mentioned value owing to the high surface area and small particle sizes of the materials.

![Figure 6. Impedance spectra of NanoFe-Fe3C-Cu at different cycles.](image1)

![Figure 7. NanoFe-Fe3C-Cu of a) Specific discharge profile of electrode at different current rate; b) Specific discharge capacity of electrode vs cycle number.](image2)

<table>
<thead>
<tr>
<th>Table I. Values of the impedance measurements.</th>
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<tbody>
<tr>
<td>Type of resistance</td>
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<tr>
<td>ohmic resistance, $R_s$ (Ω)</td>
</tr>
<tr>
<td>Charge transfer resistance, $R_{ct}$ (Ω)</td>
</tr>
<tr>
<td>Double layer capacitance, (F cm$^{-2}$)</td>
</tr>
<tr>
<td>Roughness factor</td>
</tr>
</tbody>
</table>

At 900 mA g$^{-1}$, the electrode delivered 48 mAh g$^{-1}$, which is in agreement with the galvanostatic polarization data shown in Fig. 4b).
The galvanostatic polarization shows a maximum current density of 30 mA cm$^{-2}$ at $-0.8$ V where mass transfer limits the redox process. Thus, 900 mA g$^{-1}$ is equivalent to 32 mA cm$^{-2}$, indicating that at this rate, passivation hinders the hydroxyl ion to reach the internal pore structure containing the active iron species.

To further understand the electrode process, ex-situ X-ray diffraction (XRD) analysis was carried out on the NanoFe-Fe$_3$C-Cu electrode for a fresh, formed (35 cycles) and 200 cycles in both charged and discharged states. Fig. 8a shows the XRD phase changes along the different cycles in the charged state. The following phases were observed: α-iron, Fe$_3$C, Fe(OH)$_2$, FeOOH (ICDD Powder diffraction file number (PDF numbers) : 00-006-0696, 01-075-910, 00-085-1331, 00-041-148 and 00-026-0792. The iron carbide and iron (II) hydroxide peaks showed higher intensity with the increase in the number of cycles. The increased amount of iron (II) hydroxide peak suggests that aggregation and irreversible growth of discharge products along the cycles takes place, whereas iron carbide also shows growth in peak intensities evolving in the potential region of the test system. This could suggest that thick iron hydroxide layer is formed, subsequently reducing both capacity and charge efficiency. In the meantime, the presence of magnetite was not observed due to the presence of bismuth sulfide, though less in concentration hindering its formation.

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Further analysis of the individual particles by TEM measurement was conducted on formed electrode (charged state) as shown in Fig. 9 (a-d). Fig. 9 (a and c) and Fig. 9 (b and d) are SEM images at the charge and discharge states of the electrode, respectively. Fig. 9 (a & c) clearly shows the decrease in sizes of the interconnected nano particles with high porous structure after 200 cycles. The discharged state electrode after 200 cycles in Fig. 9 (b & d) shows acicular specimen of rough iron hydroxide crystals. The cycled electrodes show negligible particle agglomeration and growth or any recrystallization of the sizes. These results confirm that the material was still in nano size structures without significant changes in the morphologies due to the specific interconnectivity between the particles of iron and iron carbide.

Fig. 8b shows the evolution of the discharged state both after formation and after 200 cycles. The following phases were observed: α-iron, Fe$_3$C, Bi, Fe(OH)$_2$ and FeOOH. The iron carbide and iron (II) hydroxide peaks showed higher intensity with the increase in the number of cycles. The increased amount of iron (II) hydroxide peak suggests that aggregation and irreversible growth of discharge products along the cycles takes place, whereas iron carbide also shows growth in peak intensities evolving in the potential region of the test system. This could suggest that thick iron hydroxide layer is formed, subsequently reducing both capacity and charge efficiency. In the meantime, the presence of magnetite was not observed due to the presence of bismuth sulfide, though less in concentration hindering its formation.

In order to understand the surface and particle size changes in the electrode, scanning electron micrograph (SEM) was analyzed and are shown in Fig. 9 (a-d). Fig. 9 (a and c) and Fig. 9 (b and d) are SEM images at the charge and discharge states of the electrode, respectively. Fig. 9 (a & c) clearly shows the decrease in sizes of the interconnected nano particles with high porous structure after 200 cycles. The discharged state electrode after 200 cycles in Fig. 9 (b & d) shows acicular specimen of rough iron hydroxide crystals. The cycled electrodes show negligible particle agglomeration and growth or any recrystallization of the sizes. These results confirm that the material was still in nano size structures without significant changes in the morphologies due to the specific interconnectivity between the particles of iron and iron carbide.

Further analysis of the individual particles by TEM measurement was conducted on formed electrode (charged state) as shown in Fig. 10 demonstrating that the particles of iron and Fe$_3$C maintain nanostructure in the size ranges of 20 to 200 nm by preserving its core-shell morphology. In the inset Fig. 10, the shell iron carbide is still visible. Interestingly, the particle morphology was not changed after the formation stage (35 cycles). Thanks to the core shell configuration, the nanostructure seems to be unchanged after cycling. Based on XRD, CV and TEM analyses, the iron carbide was not partly involved in the redox reaction at the operating potential range.

This implies that electrochemically active core and inactive shell is beneficial for the nano structure stability. It is worth to mention that previous reports related to nano iron active materials failed due to the nanoparticle agglomeration. Therefore, the capacity decay can be related to the sulfur disappearance from the electrode, which limits the discharge capacity and charging efficiency of the electrode.

Figure 8. Ex-situ XRD evolution of cycled electrode a) charged state electrode; b) discharged state electrode.

Figure 9. SEM pictures of NanoFe-Fe$_3$C-Cu electrode at different cycles (a&b after formation; c&d after 200 cycles).
Table II. Comparison of our iron electrode performance with recently reported works.

<table>
<thead>
<tr>
<th>Active materials</th>
<th>Particle size(μm)</th>
<th>Voltage window</th>
<th>Initial Discharge capacity (mAh g⁻¹)</th>
<th>Discharge rate (mA g⁻¹)</th>
<th>Reported final discharge capacity (mAh g⁻¹)</th>
<th>Cycles</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS/C</td>
<td>5-15</td>
<td>0.6 V (4 e⁻⁻)</td>
<td>325</td>
<td>300</td>
<td>322</td>
<td>100</td>
<td>28</td>
</tr>
<tr>
<td>FeS/RGO</td>
<td>5-15</td>
<td>0.6 V (4 e⁻⁻)</td>
<td>350</td>
<td>300</td>
<td>330</td>
<td>100</td>
<td>42</td>
</tr>
<tr>
<td>Fe₃P</td>
<td>0.02-0.3</td>
<td>0.5 V (4 e⁻⁻)</td>
<td>290</td>
<td>100</td>
<td>400</td>
<td>100</td>
<td>52</td>
</tr>
<tr>
<td>Carbonyl iron</td>
<td>0.5-3</td>
<td>0.3 V (2 e⁻⁻)</td>
<td>220</td>
<td>≈50</td>
<td>220</td>
<td>100</td>
<td>39</td>
</tr>
<tr>
<td>Carbonyl iron</td>
<td>0.5-4</td>
<td>0.3 V (2 e⁻⁻)</td>
<td>386</td>
<td>100</td>
<td>356</td>
<td>100</td>
<td>53</td>
</tr>
<tr>
<td>Carbon grafted iron</td>
<td>5-10</td>
<td>0.2 V (2 e⁻⁻)</td>
<td>190</td>
<td>50</td>
<td>90</td>
<td>9</td>
<td>44</td>
</tr>
<tr>
<td>Fe₃C</td>
<td>0.1</td>
<td>0.3 V (2 e⁻⁻)</td>
<td>350</td>
<td>100</td>
<td>345</td>
<td>100</td>
<td>This work</td>
</tr>
<tr>
<td>NanoFe/Fe₃C/Cu</td>
<td>0.02-0.1</td>
<td>0.2 V (2 e⁻⁻)</td>
<td>350</td>
<td>100</td>
<td>345</td>
<td>100</td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure 10. TEM pictures of Nano Fe-Fe₃C-Cu electrode after formation.

Table II shows the latest reported works on some state-of-the-art iron electrodes with different iron compounds on carbonaceous supports having disparities in particle sizes. The first three electrodes were discharged until magnetite (Eqs. 2 and 3, 4e⁻⁻) formation. In the remaining electrodes (including our work), discharge was limited until iron (II) hydroxide (Eq. 2, 2e⁻⁻) formation. It is obvious that discharging using a wider potential window or exploiting more number of electrons will consequently give more capacity. The first 3 iron electrodes exhibited around 300 to 400 mA h g⁻¹ of discharge capacity. After 100 cycles as the benchmark for comparisons, the capacity was marginally reduced from initial values. Based on the reported materials, the performance of our work shows on par with the carbon grafted iron during initial capacity, but with minimal deterioration. In addition, it was able to withstand high discharge rate operation as shown Fig. 7a and 7b.

As shown in our study, the outstanding charge and discharge performance was exhibited by copper-doped iron/iron carbide core shell type material. High surface energy of nano particles favors agglomeration, which was circumscribed in the Nano Fe-Fe₃C-Cu materials. Copper doping could provide the constant interfacial conductivity for stable electrode performance and compensates the poor electron conductor of the discharge product iron hydroxide. Furthermore, the existence of iron carbide shell prevents the agglomeration of nano particles, and thereby paving way for longer and more stable performance as well as structure stability. The double effect of both Cu and Fe₃C on the enhancement of the cyclability of the nano-iron, however, has to be investigated further in regard to the concentrations and other textural factors.

Conclusions

Core shell structured Nano Fe/Fe₃C/Cu active material was investigated as a negative electrode for application in alkaline Ni-Fe, and Fe—air batteries. This study has shown that stable electrode performance was obtained with a capacity up to 360 mA h g⁻¹ at 80% charging efficiency, even as high as 500 mA g⁻¹. Cyclic voltammetry and polarization studies showed that the presence of iron carbide and copper has improved the kinetic properties. EIS analysis gave the additional insight on the significant increase of surface roughness and decrease of the ohmic resistance. XRD and SEM results showed that there was no significant change in the crystallite sizes after major cycling studies. Though the nano particle agglomeration was prevented by the core-shell structure, sulfur dissolution was found to be the main limiting factor for the decay of the capacity. The improvements, nevertheless, makes this electrode material a viable candidate for alkaline metal-air batteries.

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References

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