Iron-based rechargeable batteries such as nickel-iron and iron-air batteries are promising candidates for large-scale energy storage applications because of their relatively low cost, inherent robustness to cycling, and eco-friendliness. In the present study, we demonstrate iron electrodes containing iron (II) sulfide and bismuth oxide additives that do not exhibit any noticeable capacity loss even after 1200 cycles at 100% depth of discharge in each cycle. In iron electrodes prepared with bismuth sulfide additive, capacity loss occurred during cycling, accompanied by a decrease in discharge rate capability and rapid passivation. The recovery of capacity by adding sulfide ions to the electrolyte confirmed that the electrode that suffered capacity fade did not have an adequate supply of sulfide ions. We also found that the loss of cycleability was accompanied by the steady accumulation of magnetite and loss of iron sulfides at the iron electrode. The use of sparingly soluble iron (II) sulfide as an electrode additive ensured a sustained and steady supply of sulfide preventing the accumulation of magnetite during cycling. Thus, we have gained understanding of the critical role of sulfide additives in achieving long cycle life in rechargeable alkaline iron electrodes.

While iron-based batteries present compelling advantages for large-scale energy storage, the extensive commercialization of these batteries has been limited by the low charging efficiency and poor discharge rate capability of the iron electrode.1 In the last four years, we have been successful in realizing extraordinarily high charging efficiency and discharge rate capability compared to the previous reports and currently-available commercial products.8,11 Recently, we have demonstrated iron electrodes with a specific capacity of 0.25 Ah/g that can be charged at an efficiency of 92% and discharged at rates up to 3C. Considering that the charging efficiency of commercial iron electrodes is just about 60–70% and the recommended discharge rate is 0.2C, the performance achieved in our electrodes represents a significant improvement.8 In the present study, we provide much needed insight into the role of the additives in improving discharge rate capability, cycle life and efficiency. To provide a background for understanding the factors governing the efficiency, discharge rate capability and cycle life, we review briefly the underlying electrochemical processes during the charge/discharge cycling of iron electrodes.

**Electrochemical equilibria at the iron electrode.**—The discharge of the iron electrode proceeds in two steps. The first step is the conversion of iron to iron (II) hydroxide (Eq. 1).

\[
\text{Fe} + 2\text{OH}^- + 2e^- \rightarrow \text{Fe(OH)}_2 + \text{H}_2\text{O} \quad E^\circ = \text{−0.877 V} \quad [1]
\]

\[
\text{Fe}_3\text{O}_4 + 8\text{H}^+ + 8e^- \rightarrow 3\text{Fe} + 4\text{H}_2\text{O} \quad E^\circ = \text{−0.912 V} \quad [2]
\]

\[
\text{Fe(OH)}_3 + e^- \rightarrow \text{Fe(OH)}_2 + \text{OH}^- \quad E^\circ = \text{−0.560 V} \quad [3]
\]

While the standard reduction potential for the formation of magnetite (Eq. 2) is close to that for the formation of iron (II) hydroxide, the latter product is favored due to the high kinetic reversibility of the reaction in Eq. 1. Iron (II) hydroxide is therefore the main discharge product of the first discharge step with the formation of magnetite favored only at very high anodic overpotentials.31,32 The second step during discharge of the iron electrode is the conversion of iron (II) hydroxide to iron (III) hydroxide (Eq. 3). The formation of iron (III) hydroxide takes place at very low potentials and this reaction is not usually utilized during the discharge of iron-based alkaline batteries.

**Charging efficiency.**—When an iron electrode is charged, the reduction of iron (II) hydroxide to metallic iron occurs according to Eq. 1. The reverse reaction occurs during discharge. The standard reduction potential for hydrogen evolution in the alkaline battery

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Inexpensive and efficient methods of storing electrical energy are essential for the successful integration of solar and wind-based electricity generation into the grid. Among the various means to store electrical energy at a large scale, batteries are particularly promising because of their advantages of high energy efficiency, modularity and flexibility to siting.1,4 The state-of-art commercially-available lithium-ion, lead-acid, nickel-metal hydride and vanadium redox flow batteries may be rated by the levelized cost of energy delivered (LCOE). LCOE is calculated as the ratio of the cost (including capital and operating costs) to the total amount of energy delivered by the battery over its useful lifetime. The LCOE for commercially-available batteries is at least five to ten times higher than the DoE targets of $0.10 to $0.20/kWh.5,6 Also, since energy storage will be required at the scale of thousands of gigawatt-hours, we are faced with the challenge of providing a sustainable solution, as the global material reserves are quite limited for these state-of-art batteries.1 Therefore, the development of inexpensive, efficient, robust and sustainable battery systems for grid-scale energy storage is a topic of intense research.3,4,6 Under an effort funded by ARPA-E, we have been focusing on developing such batteries.7,3,12

Iron-based battery systems such as nickel-iron and iron-air batteries are based on raw materials that are relatively inexpensive, globally-abundant, and eco-friendly. The promise of iron-based batteries for large-scale energy storage has spurred renewed interest in their development.11,13,16 The development of iron-based alkaline batteries began several decades ago.17–22 In the US, development of iron-air and nickel-iron batteries for electric vehicle applications was primarily undertaken by the Westinghouse Corporation and Eagle Picher Industries.18,22–25 In addition, there were several institutions worldwide that focused on the development of nickel-iron and iron-air batteries from 1970–1990.17–21 The fabrication of iron electrodes using different techniques and the strategies to improve their performance are described in numerous reports.23–28 Several fundamental aspects of the kinetics of the iron electrode and the role of various additives on the electrode performance have also been studied.29,30 Earlier reports in the literature on the performance of iron-air and nickel-iron batteries recognize the robustness of the iron electrode and the possibility of achieving up to 3000 cycles during operation.17,18,21

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The electrolyte is about 50 mV more positive to that of the iron electrode reaction (see Eqs. 1 and 4).

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad E^\circ = -0.828 \text{ V} \]  

[4]

Hydrogen evolution is therefore possible even at open-circuit on an iron electrode in alkali. Therefore, during charging, the hydrogen evolution reaction (Eq. 4) occurs in addition to the reduction reaction at the iron electrode (Eq. 1). This concomitant evolution of hydrogen can result in a low faradaic efficiency during charging. We also refer to this type of efficiency as the “charging efficiency”. As mentioned earlier, the charging efficiency of the iron electrode in commercially-available nickel-iron batteries is about 70%. Our electrodes based on high-purity carbonyl iron powder and bismuth-based additives (bismuth sulfide, bismuth oxide) can operate at charging efficiencies greater than 92%. An efficiency of 96% was measured on an iron electrode prepared with bismuth sulfide additive and corresponded to a ten-fold decrease in the amount of hydrogen evolved compared to a state-of-the-art commercial iron electrode. The high charging efficiency that we observed was attributed to the high purity of carbonyl iron and the high overpotential for hydrogen evolution on elemental bismuth produced in situ on the iron electrode.

**Discharge rate capability.**—The iron (II) hydroxide formed during discharge is electronically insulating, resulting in passivation of the electrode. Consequently, at high rates of discharge, the active material in the iron electrode is poorly utilized. In commercial electrodes, complete passivation of the iron electrode occurs even at rates of C/5, and almost no capacity is obtainable at higher discharge rates. Passivation of the iron electrode is mitigated by sulfide additives. This benefit of sulfide additives on iron electrode performance is very well known. Sulfides may be added as sparingly soluble metal sulfides to the electrode or as soluble sulfides to the battery electrolyte. Recently, we have demonstrated iron electrodes containing bismuth oxide and iron (II) sulfide additives that deliver a capacity as high as 0.2 Ah/g at the 3C discharge rate. While iron sulfides can form electrically conductive pathways to mitigate electrode passivation during discharge, further elucidation of the mechanism of de-passivation is needed. More recently, a carbon-grafted iron electrode with a high specific capacity and high discharge rate capability has been reported.

**Cycling properties of the iron electrode.**—To achieve the targeted LCOE for large-scale energy storage, the batteries must have a long cycle life. For example, at a battery cost of $100/kWh, to realize an LCOE of $0.025/kWh, about 5000 deep cycles of charge and discharge without significant loss in capacity will be required. Lead-acid batteries cannot be expected to support more than 500 cycles when subjected to cycling to 100% depth-of-discharge and operated at slightly elevated temperatures of 50°C. Similarly, lithium-ion batteries can offer about 1000–2000 deep-discharge cycles with a strict control of temperature during cycling. Consequently, the LCOE for lead-acid batteries is about $0.38/kWh, at a capital cost of $150/kWh and a round-trip efficiency of 80%. The alkaline iron electrode has been reported to be very robust to cycling, overcharge, overdischarge and elevated temperature operation. But, systematic experimental results and testing used here have been described in detail in our previous publications.

**Charging efficiency and discharge rate capability measurements.**—After fabrication, the iron electrodes were subjected to a “formation” process that involved charging and discharging the electrode repeatedly until a stable discharge capacity was obtained. During formation, the electrodes were charged at 200 mA for 2–4 hours and then discharged at 20 mA to a potential of −0.75 V (vs MMO). The charging efficiency and discharge rate capability of the iron electrodes were measured after formation was complete. The charging efficiency was measured by charging the iron electrode to its rated capacity (as measured at the end of formation) at the C/2 rate and then discharging it at the C/20 rate. The cut-off potential for the termination of discharge was −0.75 V vs MMO. The ratio of the discharge capacity to the capacity input during charge is reported here as the charging efficiency of the iron electrode. The discharge capacity was measured at rates ranging from C/20 to 1C to determine the discharge rate capability.

**Polarization studies.**—Anodic polarization experiments were performed on fully charged iron electrodes. The polarization curves were measured by conducting a potentiodynamic scan from the open-circuit potential to −0.75 V (vs MMO) at a scan rate of 0.167 mV/s.

**Cycling studies.**—After measuring the charging efficiency and discharge rate capability, the iron electrode was charged and discharged repeatedly several hundreds of times. During this extended cycling test, the electrode was charged to its rated capacity at C/2 rate and discharged at C/5 rate. A cut-off potential of −0.75 V (vs. MMO) was used to terminate the discharge. The depth-of-discharge during cycling was 100% unless specified otherwise. The phase composition following cycling was investigated by X-Ray Diffraction (XRD) measurements using a Rigaku Ultima IV diffractometer (Cu Ka source).

**Results and Discussion**

**Cycling studies.**—Two types of carbonyl iron electrodes with the following additives were studied: (1) 5% bismuth sulfide and (2) 5% iron (II) sulfide and 10% bismuth oxide.

The discharge capacity of the iron electrode containing bismuth sulfide was 0.3 Ah/g after formation, and the charging efficiency was 96%. During repeated cycling, the discharge capacity of this electrode remained stable for about 50 cycles and then began to gradually decrease. This gradual fade in the discharge capacity resulted in about 50% loss in capacity after 150 cycles (Figure 1a). However, this loss in electrode capacity was not permanent and could
be recovered completely when cycling was continued after addition of sodium sulfide to the electrolyte (Figure 1a). The sodium sulfide added was enough to reach a concentration of 2 mM in the electrolyte. Although the electrode capacity increased and stabilized after the addition of sodium sulfide, the electrode lost 60% of its capacity gradually again in 300 more cycles. This repeated loss could be recovered completely by further addition of sodium sulfide (2 mM) to the electrolyte (Figure 1a). The recovery to 100% of the capacity after the addition of sodium sulfide occurred in just 5 cycles (Figure 2).

While the iron electrode containing bismuth sulfide exhibited a capacity fade, the iron electrode prepared with iron (II) sulfide and bismuth oxide additives did not show any decrease in capacity even after 1200 cycles at 100% depth of discharge (Figure 1b). Also, these iron electrodes maintained a charging efficiency of 92% through the cycling tests. Such robustness to repeated cycling at 100% depth-of-discharge, combined with high charging efficiency is particularly attractive for deployment of energy storage at the grid-scale that will require 15 years or more of stable and efficient operation.

These results also suggested that sulfide addition in the soluble form was repeatedly needed to sustain cycle life, whereas the insoluble sulfide in the form of iron (II) sulfide was quite effective in preserving the cycling properties.

**Comparison of sulfide incorporation in iron electrodes with different additives.**—In the iron electrode prepared with bismuth sulfide additive, the electrochemical reduction of bismuth sulfide takes place during the first few charging cycles during the electrode formation process. This reduction of bismuth sulfide results in the deposition of elemental bismuth on the iron electrode and release of sulfide ions into the electrolyte (Eq. 5).

\[
\text{Bi}_2\text{S}_3 + 6\text{e}^- \rightleftharpoons 2\text{Bi}^2+ + 3\text{S}^{2-} \quad E^0 = -0.818 \text{ V} \quad [5]
\]

The sulfide ions generated as per Eq. 5, combines with the iron (II) hydroxide formed during discharge (Eq. 1) to form iron (II) sulfide on the iron electrode (Eq. 6).

\[
\text{S}^{2-} + \text{Fe(OH)}_2 \rightleftharpoons \text{FeS} + 2\text{OH}^- \quad [6]
\]

The amount of conductive iron sulfides formed in situ (Eq. 6) would depend on the amount of iron (II) hydroxide available on the iron electrode during formation, the availability of soluble sulfide by Eq. 5, and the extent of permeation of the sulfide ions into the electrode structure. During the first few cycles of electrode formation, the capacity of the iron electrode is very low and the amount of iron (II) hydroxide produced is very small. Further, the sulfide ions produced during the electro-reduction of bismuth sulfide (Eq. 5) during the first few cycles of formation will be oxidized at the nickel oxide counter electrode to sulfate, and the sulfide ions would be irreversibly depleted. Under such conditions, it is reasonable to expect that the continued in situ incorporation of iron sulfide would cease for the bismuth sulfide modified iron electrode after the initial few cycles of electrode formation. Consequently, the amount of iron sulfide formed in situ was likely to be very small relative to any deliberate additions of iron (II) sulfide at the level of 5–10 wt% of the electrode during fabrication.

In the case of the carbonyl iron electrode prepared with iron (II) sulfide additive, the high concentration and the sparingly soluble nature of the iron (II) sulfide additive provided a reservoir for sustained release of sulfide ions for a long time. Thus, the depletion of this sulfide reservoir by dissolution into the electrolyte would be a slow process. Consequently, even after 1200 cycles, the iron electrode prepared with iron (II) sulfide additive can be expected to provide adequate sulfide ions to meet the need for ensuring long cycle life and high discharge rate (Figure 1b).

Further studies were performed on the two types of iron electrodes to gain greater insight into the mechanisms underlying capacity fade and the role played by the sulfide additives on the cycling behavior.

**Change of discharge rate capability with cycling.**—For the iron electrode prepared with bismuth sulfide, the capacity achieved at any chosen discharge rate had decreased significantly after 110 cycles (Figure 3). For example, the capacity at the C/2 rate of discharge had decreased from 0.24 Ah/g to 0.08 Ah/g after 110 cycles. This level of discharge performance following capacity loss was similar to that of an iron electrode prepared without any sulfide additive (indicated as a “sulfide-free” electrode in Figure 3). However, after the addition of sodium sulfide to the electrolyte, the discharge rate capability of the electrode that had suffered capacity loss, also recovered to the values observed prior to the extended cycling studies (Figure 3).

The loss of discharge rate capability was attributed to the rapid passivation of the iron electrode. The passivation behavior refers to the maximum in the current observed during an anodic potentiodynamic scan. For a “sulfide-free” electrode, such passivation readily occurred during anodic polarization (Figure 4a). Results of such polarization studies indicated that a sulfide-free iron electrode could...
not sustain more than 0.05 A/g or a C/5 rate without undergoing passivation (Figure 4a). Prior to extensive cycling, the iron electrodes prepared with bismuth sulfide additive did not exhibit passivation, and high discharge currents could be sustained during anodic polarization (Figures 4a, 4b). These observations had suggested that sulfide was available in sufficient quantity to prevent passivation. However, after repeated cycling of the bismuth-sulfide-containing iron electrodes, a significant change in the polarization behavior was observed (Figure 4a). At an electrode potential of –0.85 V, this electrode could sustain a discharge current of only 0.15 A/g, compared to the value of 0.4 A/g before the cycling tests (Figure 4b). Thus, the capacity fade correlated well with the onset of passivation. Further, upon addition of sodium sulfide to the electrolyte of the iron electrode that had faded in capacity, the polarization characteristics were restored and higher discharge currents could be observed (Figure 4b). Therefore, we concluded that: (a) the capacity fade of the electrodes prepared with bismuth sulfide can be correlated to the electrode’s inability to be discharged at high rates, (b) the sulfide present at the start of cycling studies had been lost, and (c) the addition of sulfide to the electrolyte can mitigate passivation and restore the discharge rate capability.

Early onset of passivation and loss of discharge rate capability of the bismuth-sulfide-containing iron electrode were consistent with the results from impedance measurements performed during the cycling studies (Figure S1). The low-frequency impedance of the iron electrode that had faded in capacity was higher than an electrode that had not shown capacity fade. After the addition of sodium sulfide to the faded electrode, the increase in discharge capacity was accompanied by a decrease in the electrode impedance at low frequencies.

Overpotentials during constant current charging.— The electrode potential during charging was monitored during cycling for the two types of electrodes, namely: (1) carbonyl iron with bismuth sulfide and (2) carbonyl iron with bismuth oxide and iron (II) sulfide additives (Figure 5). The behavior of the two types of electrodes was considerably different. The overpotential during charging for the iron electrode prepared with bismuth sulfide additive increased gradually with cycling over 100 cycles. Specifically, the overpotential for the electrode formulated with bismuth sulfide increased by more than 100 mV.
in 100 cycles at 50% state-of-charge (Figure 6). This change in overpotential was accompanied by a 40% loss in discharge capacity (Figure 1a). However, the overpotential at 50% state-of-charge for the iron electrode containing bismuth oxide and iron (II) sulfide additives did not increase even by 5 mV after 1200 cycles (Figure 6), remarkably different from the electrode prepared with bismuth sulfide additive.

An increase of overpotential during charging as seen in Figure 6 with the electrodes prepared with bismuth sulfide suggested that the polarization resistance for charging increased as cycling proceeded. Such a gradual increase of polarization resistance can occur if iron is discharged to a poorly reversible phase such as magnetite, Fe₃O₄. During discharge of an iron electrode, in addition to iron (II) hydroxide (Eq. 1), the iron (II, III) oxide, magnetite (Fe₃O₄) can also be formed (Eq. 2):

\[
\text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} + 8e^- \rightleftharpoons 3\text{Fe} + 8\text{OH}^- \quad E^0 = -0.912 \text{ V} \quad [2]
\]

From the relative values of the standard electrode potentials, the formation of magnetite is more favorable compared to iron (II) hydroxide. However, the kinetic reversibility of the reactions in Eq. 1 facilitates the formation of iron (II) hydroxide during electrode discharge.23,32 Towards the end of discharge, at electrode potentials close to the cut-off value of −0.75 V vs. MMO, the overpotential is sufficiently high to lead to the formation of magnetite (Eq. 2). Magnetite is a semiconductor with an electronic conductivity of 10⁻⁸ to 10⁻⁷ S cm⁻¹.44 However, the overpotential for the reduction of magnetite to metallic iron is very high and attempts to reduce magnetite in alkaline media results in mainly hydrogen evolution.47 Under similar conditions as investigated here, the faradaic efficiency of the reduction of magnetite to iron has been reported to be less than 20% with hydrogen evolution consuming most of the input charge.47 A gradual buildup of the poorly-rechargeable magnetite phase on the iron electrode could result in a decrease in the cycleable active material and an increase of polarization resistance and overpotential during charging at constant current (Figure 5a and Figure 6). Thus, as the iron electrode was discharged repeatedly up to −0.75 V, the amount of Fe₃O₄ formed at the iron electrode could gradually increase in each cycle.

The X-ray diffractogram of the iron electrode prepared with bismuth sulfide additive and subjected to several cycles of charge and discharge confirmed the presence of magnetite in the electrode (Figure 7). We have also found reports in the literature of the formation of magnetite on iron electrodes when cycled between electrode potentials close to the cut-off value of −0.75 V vs MMO, indicating over a ten-fold increase in the amount of magnetite converted to metallic iron in the presence of sulfide. We concluded that in the presence of sulfide ions, the poorly reversible magnetite phase underwent reduction to form metallic iron during electrode charging. Thus, when sulfide was not present in adequate amounts, the relatively irreversible magnetite phase gradually accumulated in each cycle leading to the observed capacity fade of the carbonyl iron electrode. The X-ray diffractogram of this iron electrode with bismuth sulfide additive also does not show any iron sulfide peaks (Figure 7). This is in contrast to an iron electrode with similar composition where mixed valence iron sulfides were observed within a few cycles after electrode formation (Figure S2).8 Thus, the accumulation of magnetite in the electrode coincided with the loss of iron sulfides from the bismuth sulfide modified iron electrode.

The potential-charge curves of the iron electrode prepared with bismuth sulfide additive that had lost capacity showed two well-defined potential regions (Figure 9) corresponding to the iron electrode reaction (−1.1 V to −1.2 V vs MMO) and hydrogen evolution (−1.3 V vs MMO). Upon addition of sodium sulfide to the electrolyte, the charge corresponding to the iron electrode reaction increases in preference to investigated the rechargeability of the magnetite phase in the presence of sulfide ions. To this end, we performed independent experiments on magnetite electrodes prepared by pressing a mixture of magnetite with polyethylene binder (20 wt%) and acetylene black (10 wt%) on a nickel grid. The magnetite electrode was charged at a constant current of 75 mA in potassium hydroxide electrolyte (30 wt%) for 20 hours. Subsequently, the electrode was discharged at 15 mA until a cut-off voltage of −0.75 V (vs MMO) was reached. Similar charge and discharge studies on the magnetite electrode were performed after the addition of 2 mM sodium sulfide to the potassium hydroxide electrolyte. We found that the discharge capacity increased from 9 mAh to 120 mA in the presence of sulfide ions in the electrolyte (Figure 8), indicating over a ten-fold increase in the amount of magnetite converted to metallic iron in the presence of sulfide. Thus, when sulfide was not present in adequate amounts, the relatively irreversible magnetite phase gradually accumulated in each cycle leading to the observed capacity fade of the carbonyl iron electrode. The X-ray diffractogram of this iron electrode with bismuth sulfide additive also does not show any iron sulfide peaks (Figure 7). This is in contrast to an iron electrode with similar composition where mixed valence iron sulfides were observed within a few cycles after electrode formation (Figure S2).8 Thus, the accumulation of magnetite in the electrode coincided with the loss of iron sulfides from the bismuth sulfide modified iron electrode.

Charge and discharge studies on magnetite electrodes.— We recall here that cycling is accompanied by an increasing tendency for the electrode to be passivated, resulting in loss of discharging rate capability (Figures 3, 4a). We also found that the discharge capacity of a faded iron electrode can be recovered completely by the addition of sodium sulfide to the electrolyte (Figure 1a). Therefore, we...
Effect of sulfide addition on the charging characteristics of an iron electrode that has faded in capacity. Potential – Charge curves measured on a bismuth sulfide modified iron electrode during charging before and after the addition of sodium sulfide to the electrolyte.

After about 8 cycles, the amount of charge diverted to hydrogen evolution is minimal and the iron electrode reaction takes up almost all the input charge. Correspondingly, the overpotential for charging decreased steadily in every cycle after the addition of sodium sulfide to the electrolyte. This reduction in overpotential was almost 100 mV, and the electrode potential returned to values that were observed before any capacity loss occurred (Figure 9).

The evidence of magnetite on an iron electrode that has suffered capacity fade, the effect of added sulfide on the charging overpotentials, and the increased rechargeability of magnetite in the presence of sulfide, pointed to the slow accumulation of the poorly rechargeable magnetite phase as the underlying cause of capacity fade.

Effect of overcharge and charge rate on the recovery of capacity.—If the accumulation of poorly rechargeable magnetite was the cause of capacity loss, we could expect extended overcharge or a slow rate of charge to aid recovery of the lost discharge capacity. To verify the benefit of overcharge, the electrode that had suffered capacity loss was periodically overcharged once in every 10 to 15 cycles to the extent of 100% at the C/2 rate. Following such overcharge we found that the discharge capacity of the electrode was always higher than with the experiments without any overcharge (Figure 10). Also, when the charge rate was lowered from C/2 to C/10, we observed a further increase in discharge capacity (Figure 11). A decrease in the rate of capacity fade was also observed for an overcharge of 100% at a reduced charge rate of C/10 (Figure 11). These observations were consistent with accumulation of the poor rechargeable magnetite phase that was slowly converted to iron during prolonged overcharge at a low rate. Accordingly, higher rates of charging resulted in return of a lowered value of discharge capacity. For example, when the charging rate of the iron electrode was increased from C/5 to 2C during cycling, a decrease in discharge capacity was observed (Figure 12). Yet, the high charging rate did not affect the rate of capacity fade. When charging at rates as high as 2C, the parasitic hydrogen evolution reaction became more favorable. Consequently, the charging efficiency of the iron electrode decreased and a lower value of capacity was returned during discharge. This decrease in the value of discharge capacity resulting from the increased charge rate was not a permanent loss and could be recovered simply by charging at a lowered rate of C/2 (Figure 12).
Effect of discharge rate on the recovery of capacity.— Experiments were performed by fixing the charging rate at C/2 and conducting the discharge at C/5 or 1C rate (Figure 13). When an electrode that had suffered capacity fade was cycled repeatedly at 1C rate of discharge, a rapid decrease in the discharge capacity was observed (Figure 13). After several cycles at the 1C rate, when the discharge rate was decreased to C/5, a full recovery of capacity was observed (Figure 13). Thus, operating at low discharge rates reduced the apparent rate of capacity fade. However, despite the recoverability of discharge capacity at low discharge rates, a slow increase of overpotential of the electrode during charging was still evident, indicating the formation of the less reversible magnetite phase during the cycling (Figures 13 and 14).

Effect of depth of discharge (DoD) on capacity fade.— Despite the robustness of the iron electrode to mechanical stresses induced by deep discharge, we found that in the absence of adequate sulfide ions the capacity fade depended strongly on the depth of discharge (DoD) similar to other rechargeable batteries.33,48 We observed that when cycled at 83% DoD, the discharge capacity of the iron electrode prepared with bismuth sulfide additive decreased by 26% after about 300 cycles. This rate of capacity fade at 83% DoD is much lower than the fade rate at 100% DoD when a 25% loss in capacity occurred within 100 cycles (Figure 15).

Comparison of the cycling behavior of iron electrode with different additives.— We also recognize that depending on how the sulfide additives are incorporated in the electrode, significant differences in performance can result. In the case of the iron electrode prepared with bismuth sulfide additive, these conductive iron sulfide phases are formed in situ during the electrode formation process. However, in the case of the iron electrode prepared with iron (II) sulfide additive, the slow release of sulfide ions resulting from the sparingly soluble nature of iron (II) sulfide provided the necessary de-passivating properties during discharge. The iron sulfides are characterized by a very low solubility constant and therefore are not expected to be rapidly removed from the iron electrode (Eq. 7).49

\[
\text{FeS} \rightleftharpoons \text{Fe}^{2+} + \text{S}^{2-} \quad K_{eq} = 4 \times 10^{-19} \quad [7]
\]

In the iron electrode prepared with bismuth sulfide, a limited amount of iron is sulfide is formed in situ and consequently, the benefit of sulfide is lost in a few cycles. Thus, in about 150 cycles, the iron electrode prepared with bismuth sulfide additive lost nearly 50% of its capacity. Similarly, a gradual loss in capacity in about 100 cycles following formation has been observed by Shukla et al. with in situ carbon-grafted iron electrode prepared with bismuth sulfide additive.13

In the case of the iron electrode with bismuth sulfide additive, the loss of the in situ formed iron sulfides and the accumulation of magnetite during repeated cycling manifests in a loss of electrode capacity (Figure 17a). The addition of sodium sulfide to the electrolyte of this electrode leads to capacity recovery in the short term (Figure 17a). The reaction of dissolved sulfide with iron (II) hydroxide should result in the formation of some iron sulfide. The iron sulfides so produced could be poorly distributed throughout the electrode structure to provide a long-term benefit, and consequently, capacity fade is observed again in about 100 cycles.

When iron (II) sulfide was added to the carbonyl iron electrode as an additive during electrode fabrication, a sustained supply of sulfide within the iron electrode structure was ensured. The consistent
Figure 17. Schematic of the cycling behavior of a carbonyl iron electrode with (a) bismuth sulfide additive and (b) iron (II) sulfide + bismuth oxide additives.

presence of sulfide prevented the accumulation of magnetite phase by facilitating its reduction to metallic iron during charging (Figure 17b) and resulted in an iron electrode with long cycle life.

As the leaching of the sulfides from this iron electrode will deplete the reserves, albeit slowly, we could adjust the amount and distribution of iron (II) sulfide in the original electrode for achieving the desired cycle life.

Conclusions

The carbonyl iron electrode prepared with iron (II) sulfide and bismuth oxide additives did not show any capacity fade for more than 1200 cycles of charge and discharge at 100% DoD. However, an iron electrode prepared with bismuth sulfide additive showed about 50% loss in capacity after 150 cycles. This capacity loss was recovered by the addition of sodium sulfide to the electrolyte, but the slow decay in capacity was found to persist even after the addition of sulfide ions.

We have confirmed that the capacity fade in the iron electrode was due to the formation of a poorly reversible magnetite phase on the iron electrode during discharge. During repeated cycling, the amount of this relatively irreversible magnetite phase in the electrode increased, resulting in a loss of capacity. Iron sulfides were also no longer present in the electrode that had suffered capacity fade. The accumulation of magnetite also results in increase of charging overpotential. We were able to show that re-charging the magnetite phase to iron is facilitated by the presence of sulfides. Consequently, the addition of sodium sulfide to the electrolyte of a faded electrode results in capacity recovery. However, the effect of these sulfide ions is lost in about 200 cycles as the free sulfide in the bulk of the electrolyte is oxidized quite readily at the nickel oxide counter electrode. The capacity lost could also be recovered by overcharging the electrodes at a slow rate that allowed the magnetite phase to be converted to iron. However, this process would have to be repeated periodically to retain electrode performance. This observation is consistent with literature reports that frequent overcharge improves retention of electrode capacity.

When the sparingly soluble iron (II) sulfide is added to the electrode in substantial quantities in the range of 5 to 10 weight %, a sustained and slow release of sulfide is ensured for a long time, and this allows over 1200 cycles to be achieved without loss of capacity. In the absence of sufficient sulfide, by limiting the depth of discharge, a capacity reserve of cycleable active material is retained, delaying the observed onset of capacity fade despite the formation of magnetite in every cycle.

When sulfide was added to the electrolyte, the high discharge rates could be sustained. However, as sulfides were depleted by oxidation at the counter electrode, rapid passivation was found to limit the capacity output. With the electrodes of low sulfide content, rapid passivation of the electrode was observed at high rates of discharge. The depassivation provided by the sulfides was found to be essential in ensuring good discharge rate capability.

In summary, these studies revealed the critical role of sulfide in retaining capacity output and discharge rate capability over extended cycling periods. The role of sulfide additives in the discharge of the iron electrode is two-fold. Firstly, a conductive phase of iron sulfides prevents the rapid passivation of the iron electrode during discharge. Secondly, the sulfide ions reduce the overpotential for the conversion of magnetite to metallic iron during charging. Presence of sulfide ions in the electrode is therefore critical to prevent the accumulation of the poorly rechargeable magnetite phase on the electrode during cycling. When the concentration of sulfide-ion generating materials in the electrode decreases during cycling, the ability to recharge magnetite to metallic iron decreases, resulting in capacity fade (Figure 1a). We have been able to prove that such a capacity fade is readily reversed by the addition of sodium sulfide to the electrolyte. Therefore, the distribution and concentration of sulfide ions in the electrode is crucial not only as a de-passivation additive but also for the capacity output of the electrode during long-term cycling. Sparingly soluble sulfide such as iron (II) sulfide added to the electrode appeared to be the best expedient in limiting the loss of sulfides during cycling, and ensuring the longevity of the electrode performance.

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