Alkaline iron electrodes present some challenges for use in secondary batteries that are associated with low coulombic efficiency and discharge utilization. Low coulombic efficiency is correlated to the hydrogen evolution reaction that takes place during charge. In this work, we demonstrate rechargeable alkaline iron electrodes with significant capacity retention over 150 cycles with high efficiency by suppressing the hydrogen evolution with stannate. Adding stannate to the alkaline electrolyte when cycling the iron electrode drastically changes the electrochemistry. The additive brings on two advantageous attributes for the iron electrode: increased hydrogen evolution overpotential, and a flat and prolonged discharge curve at typical battery operation. These attributes were provided by a novel intermediate phase that was detected from in situ neutron diffraction measurements. This phase was only detected in situ while decomposed ex situ, and indicated a solid solution constituted by some of the elements present in the electrode.

The Fe electrode is thermodynamically unstable at the open circuit potential. The hydrogen gas, H$_2$, evolution reaction is more favorable in aqueous electrolyte according to Reaction 4:

$$H_2(g) + 2OH^- \rightarrow 2H_2O(l) + 2e^-$$

$E^\theta = -1.17$ V vs. Ag/Ag$_2$O [4]

Moreover, Fe metal is a good H$_2$ evolution catalyst which is a major concern. When the Fe electrode is reduced it will simultaneously evolve H$_2$ gas, hence reducing the charging efficiency. Another drawback of the Fe electrode is the passivation layer that builds up over time. The passivation layer consists of corrosion products and contains a number of different oxidized iron phases, specifically, Fe(OH)$_2$, Fe$_3$O$_4$, and hematite, Fe$_2$O$_3$.

It is critical to suppress the H$_2$ evolution and to break down the passivation layer in order to exhibit good reversibility and high round-trip efficiency.

The Fe electrode was first used as an anode in the alkaline Ni-Fe battery, developed by the Edison Company, at the beginning of the 20th century. Despite the fact that the Fe electrode has been known and used for over a century, it suffers from long-term inefficiency. The Fe electrode faces two major obstacles: low coulombic efficiency due to parasitic side reactions and buildup of a passivation layer when cycling the battery. Thus, the conventional Fe electrode exhibits an unsatisfactory round-trip efficiency and energy density. The conventional Fe electrode reaches a charging efficiency of 60–70% at a discharge rate of 0.2 C. As a background to the limitations of the Fe electrode, we provide a brief description of its redox chemistry.

The redox chemistry of the Fe electrode in the alkaline battery depends on the depth-of-discharge (DOD). The Fe electrode undergoes two discharge steps: the first step involves the two-electron transfer of iron to ferrous hydroxide, Fe(OH)$_2$, with a theoretical capacity of 962 mAh g$^{-1}$, and the second step is a further oxidation of Fe(OH)$_2$ to either magnetite, Fe$_3$O$_4$, or to iron oxyhydroxide, FeOOH, with a theoretical capacity of 199 and 298 mAh g$^{-1}$, respectively. The charge and discharge reactions of the Fe electrode can be described by the Reactions 1, 2, and 3. Their standard electrode potentials are given with respect to Ag/Ag$_2$O (0.343 V vs. SHE):

$$\text{Fe} (s) + 2OH^- \rightarrow \text{Fe} (OH)_2 (s) + 2e^-$$

$E^\theta = -1.22$ V vs. Ag/Ag$_2$O [1]

$$3\text{Fe} (OH)_2 (s) + 2OH^- \rightarrow \text{Fe}_3\text{O}_4 (s) + 4H_2O (l) + 2e^-$$

$E^\theta = -1.00$ V vs. Ag/Ag$_2$O [2]

$$\text{Fe} (OH)_2 (s) + OH^- \rightarrow \text{FeOOH} (s) + H_2O (l) + e^-$$

$E^\theta = -0.90$ V vs. Ag/Ag$_2$O [3]

$$H_2 (g) + 2OH^- \rightarrow 2H_2O (l) + 2e^-$$

$E^\theta = -1.17$ V vs. Ag/Ag$_2$O [4]

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dissolve to generate stannate-ions, Sn(OH)₆³⁻ which can be reduced to Sn by Reaction 5:²¹

\[ Sn(OH)_6^{3-} + 4e^- \leftrightarrow Sn(s) + 6OH^- \]  

\[ E^0 = -1.26 \text{ V vs. Ag/Ag}_2O \]  

We investigated the effect of the K₂SnO₃ on the rechargeable alkaline Fe electrode, both ex situ and in situ, by electrochemical, morphological and phase evolution characterization. We observe stable capacity retention over 150 cycles with the use of stannate. The additive provides an increased hydrogen evolution overpotential and prolonged character of the Fe electrode discharge curve which both are desirable in the real life battery application. With the use of in situ neutron diffraction we investigate the phase evolution upon charge and discharge cycling by collecting diffraction data while simultaneously making electrochemical measurements. From this, we observed a novel intermediate phase when K₂SnO₃ was added to the Fe electrode and correlated its phase evolution to the state-of-charge (SOC).

**Experimental**

**Cell preparation.**—The Fe electrodes were prepared by mixing 80 wt% Fe powder (Nutrafine RS, Höganas AB), 5 wt% Bi₂S₃ (Sigma-Aldrich), 8 wt% graphite (Imerys Energy KS6L), 2 wt% carbon black (Imerys Super C65), 5 wt% polytetrafluoroethylene binder (PTFE 60 wt% dispersion, Sigma-Aldrich). The mixture was worked into a slurry by using a mortar and pestle and a small amount of ethanol. The slurry was mechanically worked into a paste that was rolled onto a flat surface using a rolling pin. The rolled out paste was prepared with a thickness of 0.1 mm and dried for 1 h at 110°C. The thin film was pressed onto a nickel, Ni mesh (100 mesh, Dextem Corporation) using a uniaxial press at 30 MPa. A scanning electron microscopy (SEM) image of the Fe powder is shown in the supplementary information Figure S1.

In all electrodes a Ni mesh was used as current collector except in the charge and discharge cycle experiment without K₂SnO₃, here a copper, Cu, mesh (60 mesh, Dextem Corporation) was used as current collector. Thin strips of Ni foil (60 μm thickness) were spot welded onto the Ni or Cu mesh to provide current connection. Conventional sintered Ni electrodes (supplied by Dr. Phil Bennett, Gates Energy) served as counter electrode in all cells. An Ag/AgClO₄ reference electrode (+0.34 V vs. SHE) was used and the assembly of it is described in the supplementary information. The two electrodes were separated with one layer of nonwoven cellulose membrane (700/18F, Freudenberg), sandwiched between two acrylic pieces, and sealed with paraffin. The cell was flooded with 30 ml electrolyte.

**Electrochemical characterization.**—A 6 M KOH (Sigma-Aldrich) + 1 M LiOH (Fluka) mixture was used as alkaline electrolyte. The alkaline electrolyte with stannate included 0.1 M K₂SnO₃ (Sigma-Aldrich). The cyclic voltammetry measurements were carried out in a three electrode setup and controlled by a potentiostat (BioLogic SP-50). The charge and discharge cycle study used a computer controlled current source (CT2001A, Wuhan LAND Electronics). The solution resistance was evaluated for the three-electrode setup by the current interrupt method before starting an experiment. The solution resistances obtained (1–13 Ω) were neglected because of their insignificant effect on the measured potential. Cyclic voltamograms (CVs) were prepared by sweeping the potential between −1.4 and −0.7 V vs. Ag/AgClO₄ with a scan rate of 200 μVs⁻¹. The cyclic voltammograms were characterized and discharged at a C/5 rate based on the two electron transfer theoretical specific capacity of 962 mAh g⁻¹ corresponding to a rate of 192.4 mAh g⁻¹. A rest step of 10 min between each step was used and -1.4 and -0.7 V vs. Ag/AgClO₄ voltage cutoffs were used for the charge and discharge, respectively.

**Post-mortem characterization.**—For post-mortem analysis, the Fe electrodes were rinsed in deionized (DI) water and dried for 1 h at 110°C. To quantify the elemental composition, SEM images were recorded with a JSM-7000F field emission microscope (JEOL) integrated with energy dispersive X-ray spectroscopy (EDS). X-ray diffraction (XRD) patterns were obtained with a X’Pert Pro powder diffractometer (PANalytical) at ambient conditions. Play-Doh clay was used to hold the Fe electrodes during the measurement. X-ray photoelectron spectroscopy (XPS) was performed on ULVAC-PHI Versaprobe 5000 spectrometer using monochromatic Al Kα line (1486.6 eV) as X-ray source. The radiation was set at 25 W nominal power with a beam size of 100 μm × 45° measurement angle. The samples studied were charge neutralized by a dual system consisting of low energy electrons and Ar⁺ ions. The spectrometer energy scale was calibrated with two reference points: Au4f7 at 84 eV and Cu2p3 at 932.7 eV. The pass energy was set to 187.85 eV and a scanning step size of 1 eV for the survey spectrum. The pass energy was changed to 23.5 eV and the scanning step size was changed to 0.1–0.2 eV when individual elements were measured.

In situ neutron diffraction data collection and structure refinement.—The electrochemical cell for the operando neutron diffraction measurement has been described elsewhere.²² The Fe electrode was prepared in the same way as in the cell preparation section and the amount of Fe powder used was 1.25 g. The positive electrode consisted of Ni mesh only and O₂ and D₂ gas was evolved when the cell was charged and discharged, respectively. To minimize the incoherent scattering contribution from H nuclei, which would contribute a significant background to the neutron diffraction patterns, 3 ml of 6 M KOD and 0.1 M K₂SnO₃ electrolyte was used in the cell. No membrane was used to separate the electrodes; instead physical separation with a 5 mm distance between the two electrodes was provided. Prior to the in situ measurement, the Fe electrode was cycled galvanostatically against O₂/D₂ until a stable discharge capacity was achieved. The Fe electrode was cycled at C/10 rate, 60% DOD charging step based on the two electron transfer reaction, −1.2 V voltage cutoff at discharge, and 30 min of rest between each step. The specific discharge capacity achieved after 19 cycles was 420 mAh g⁻¹. The cell, in a fully discharged state, was then disassembled. The Fe electrode was taken out and rinsed with D₂O and then dried under vacuum. Finally, the cell was reassembled for the in situ neutron diffraction measurement and refilled with 3 ml of fresh electrolyte. Time-of-flight powder neutron diffraction data were collected on the Polaris diffractometer at the ISIS pulsed spallation neutron source, Rutherford Appleton Laboratory, UK.²³ A series of diffraction patterns were collected each of 60 min duration in order to ensure good statistical quality. The cell was charged for 5 h at C/10 rate before the in situ measurement, then cycled once at C/10 rate for 5 h during discharge with 30 min rest step subsequently, and finished with charge for 4 h at C/5 rate. Only the data from the low angle detector bank (40° < 2θ < 67°, dmax = 7 Å, Δd/d = 0.86%) was used for Rietveld analysis with GSAS as this contains the necessary range of Bragg reflections for identification of all phases.²⁴ The Bragg peak profile was described by a Pseudo-Voigt function (function 3 in GSAS)²⁴ and only the Gaussian width of the function was refined.

**Results and Discussion**

Electrochemical characterization.—CVs were prepared to achieve a fingerprint of the redox chemistry involved in order to correlate them with the structural changes in the Fe electrode during cycling. The reduction and the oxidation of the Fe electrode was controlled by a potential sweep and the upper and lower potential limits were set to the redox chemistry between Fe⁰/Fe⁶⁺. The CVs are shown in Figure 1 and all data were normalized to the active mass of Fe.

In the first cycle of both samples, the Bi₂S₃ underwent a reduction to Bi⁰ and S²⁻ according to the following reaction:²⁵

\[ Bi₂S₃(s) + 6e^- \leftrightarrow 2Bi⁰(s) + 3S²⁻ \]  

\[ E^0 = -1.26 \text{ V vs. Ag/AgClO}_4 \]  

The reduced Bi⁰ left S²⁻ to be adsorbed onto the Fe electrode. The adsorbed S²⁻ enhanced the reversibility of the Fe electrode by
Fe electrodes without and with K₂SnO₃ presented different trends. In the former sample, the specific capacity (the specific capacity is the area underneath the curve with the unit mAh g⁻¹ and normalized to the active Fe mass) increased after 20 cycles, whereas in the latter sample, the capacity decreased after 20 cycles. The unstable redox chemistry when K₂SnO₃ was added might be due to the active dissolution of Sn metal to Sn(OH)₄²⁻ first, and followed by the transformation to Sn(OH)₆⁵⁻.²⁷

The Fe electrodes without and with K₂SnO₃ were assembled and tested in flooded cells by galvanostatically charge and discharge cycle them at a moderate rate (C/5). Both cells were deep discharged, meaning they were oxidized to the second plateau that corresponded to the formation of Fe₂O₃. In contrast, commercial alkaline Fe electrodes limit the discharge to the first plateau corresponding to the formation of Fe(OH)₂.² Cells were prepared to study the effect of the additive and the results are shown in Figure 2.

The specific discharge capacity as a function of cycle number of the two samples without and with K₂SnO₃ is shown in Figure 2a. An increase of capacity was achieved for both samples over the first 30 cycles. This increase in capacity was described by Manohar et al. as the formation step caused by the gradual penetration of electrolyte to the core of the Fe particles in the dissolution and precipitation Reaction 1.¹¹ The formation of the Fe electrodes showed a similar trend where the discharge capacity increased to a certain point, decayed and lastly stabilized. The specific capacity of the Fe electrodes stabilized around 400 and 250 mAh g⁻¹ for the samples without and with the additive, respectively. The charge and discharge curves of the two samples are shown in Figures 2b and 2c. Voltage cutoff was used during charge at −1.4 V to avoid continuous reduction of Sn metal from the excess Sn(OH)₆²⁻ ions in the electrolyte. The coulombic efficiency of the sample without the additive was not considered because the cell was overcharged to 500 mAh g⁻¹ for each cycle and never reached the upper voltage limit at −1.4 V. However, with K₂SnO₃ the charge curve was shifted to more negative potentials because of the increased H₂ overpotential. The resultant coulombic efficiency after the formation step (>30 cycles) was 85.3 ± 4.8%. The amount of H₂ was not measured in this work. The observed electron transfers in both charge (reduction) and discharge (oxidation) of the Fe electrodes were comparable to the results obtained from the CVs. A noteworthy observation was the prolonged discharge plateau at −1.1 V for the Fe electrode with the additive. If the specific discharge capacity for the first plateau was directly compared between the two samples, the Fe electrode with the additive outperformed the one without (220–260 mAh g⁻¹ vs. 125–180 mAh g⁻¹).

Post-mortem characterization.—Post-cycled Fe electrodes without and with K₂SnO₃ were characterized. A pristine Fe electrode was included in the study as comparison. The structural effect of the K₂SnO₃ on the Fe electrode was the important objective and if metallic Sn was detectable on the surface. SEM images of the electrodes, one pristine and two post-cycled without and with the additive, are shown in Figure 3.

In the pristine electrode in Figure 3a, Fe particles with an average diameter of 10 μm are observed (SEM image of the Fe powder is shown in the supplementary information Figure S1). Graphite flakes settled in the backbone and 40–60 nm carbon black particles are observed. Cycling reduced the size of the active particles to an average size of 0.2–1 μm c.f. Figures 3b and 3c. We attribute the reduction in particle size to the dissolution and precipitation Reaction 1.¹⁵ The morphological difference between the Fe electrodes, without and with the additive, was not clear. Cubic crystals with the particle size of 0.2–0.4 μm was evident in both images. However, larger tetragonal crystals with particle size of 0.6–1 μm were observed in the latter sample. EDS measurements confirmed an averaged 3.1 wt% Sn in the surface of Figure 3c. Spot analysis with EDS showed that Sn was concentrated on the bigger tetragonal crystals in Figure 3c. The composition of Figure 3b from the EDS data was: 23.9 wt% C, 26.9 wt% O, 45.1 wt% Fe and 4.1 wt% Bi. The elemental composition of Figure 3c of the EDS data was: 58.0 wt% C, 14.7 wt% O, 22.4 wt% Fe, 23.9 wt% C, 26.9 wt% O and 45.1 wt% Fe and 4.1 wt% Bi.
Fe, 1.90 wt% Bi and 3.0 wt% Sn. No S was detected. The high content of oxygen measured was mainly from the Fe$_3$O$_4$ and was the result of inactive sites formed upon cycling or the result of Fe oxidation after rinsing the electrode.

Powder XRD patterns from the electrodes are shown in Figure 4. The peaks were identified and labelled with their corresponding phase with the help of the PDF database.28

No current collector was used for the pristine electrode and only the electrode paste consisting of Fe, Bi$_2$S$_3$, graphite, carbon black and PTFE was measured. As expected, the peaks for the pristine electrode corresponded to the three main crystalline phases: Fe, Bi$_2$S$_3$ and C. In the cycled Fe electrode without the additive, the crystalline phases detected were: Fe, Fe$_3$O$_4$, C, Bi and Cu (used as current collector), whereas the cycled Fe electrode with the stannate additive consisted of the same crystalline phases—but with Ni (used as the current collector) instead of Cu—plus the Play-Doh clay and Sn. An XRD pattern of the clay is shown in the supplementary information Figure S2 and corresponded to the observed peaks (label “x”) shown in Figure 4. Detection of Sn metal was confirmed from the XRD pattern in agreement with the EDS measurement. The similar relative intensity ratio

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**Figure 2.** Galvanostatic charge and discharge cycling of Fe electrodes without and with K$_2$SnO$_3$ at C/5 rate. a) Cycle summary of the two samples over 150 cycles, b) charge and discharge curves of the Fe electrode without K$_2$SnO$_3$ vs. Ag/Ag$_2$O, c) charge and discharge curves of the Fe electrode with 0.1 M K$_2$SnO$_3$ vs. Ag/Ag$_2$O.

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**Figure 3.** SEM images of a) pristine Fe electrode, b) Fe electrode cycled 150 times at fully charged state and c) Fe electrode cycled 150 times with 0.1 M K$_2$SnO$_3$ at fully charged state. The magnification was 10000x with a working distance of 10.0 mm for all images.
between Fe₃O₄ and Fe in both post-cycled Fe electrodes indicated that all active material was not fully reduced. This was in accordance to the high content of oxygen detected from the EDS measurements.

XPS measurements were carried out on the post-cycled Fe electrode with K₂SnO₃ to verify the deposition of Sn on the surface. Survey scan of the Fe electrode from a depth of 5 nm is shown in the Figure 5a. From the XPS spectrum, six elements were observed: C, O, Bi, F, Sn and Fe. S and K were not detected. The signal from Fe was weak and as it was close to the F1s peak. The weak signal of Fe indicated only a minor content on the surface.

High resolution spectra of the individual elements are presented in the Figures 5b–5f. According to the fitted XPS data, the surface of the sample was mainly a mixture of C, PTFE, Bi₀.₅F₂, Bi₂O₃, SnO₂ and Fe₃O₄. Most important was the detection of SnO₂ resulting from oxidation under exposure to air and confirmed the deposition of Sn. Synthesis of Bi₀.₅F₂ was likely taking place during the sample exposure to the X-ray radiation. The formation of Bi₀.₅F₂ was supported by comparing C1s, F1s and Bi4f spectra (supplementary information Figure S3) after relatively short time acquisition (1 cycle) and five times longer acquisition time (5 cycles) on the same spot. The data showed that after longer acquisition time, the amount of PTFE was decreased, whilst the amount of carbide was increasing. F released from the PTFE was reacting with Bi and resulted in an increase of the Bi₀.₅F₂ phase. At the same time, the electron distribution of F bounded to C was changing and was observed as a shift toward lower energy values in Figure S3c.

In situ neutron diffraction data collection and structure refinement.—In situ neutron diffraction measurements were conducted using an electrochemical cell designed especially for the Polarisc instrument at ISIS.²²,²⁹ Prior to the measurement, the Fe electrode was activated by galvanostatically charge and discharge cycling in deuterated 6 M KOD and 0.1 M K₂SnO₃ electrolyte. The electrochemical results are shown in the supplementary information Figure S4. A stable specific discharge capacity of 420 mAh g⁻¹ was achieved after 19 cycles of deep discharge (to second discharge plateau) and overcharge (charged for 500 mAh g⁻¹ each cycle). The specific discharge capacity was in agreement with the Fe electrode shown in Figure 2b except that the number of cycles needed to activate the electrode was less because a slower rate (C/10 vs. C/5) was used. No significant overpotential shift over 19 cycles was apparent and the expected electrochemical behavior of the Fe electrode was also obtained in the in situ neutron scattering cell. Representative patterns at the fully charged state of the cell and the Rietveld refinement fit to the data are shown in Figure 6. The data collected from the cell included the Fe electrode, the Ni current collectors and Ni mesh.

The background contribution from the amorphous/liquid components in the cell was small and could be modeled using a shifted Chebyschev function with 12 variable parameters. In the initial stages of the refinement, the following phases were included: Ni, Fe, Fe₃O₄ (including both the nuclear and the magnetic scattering), C, and Bi. Ni peaks from the cell construction dominated the pattern. C and Bi were also present but the contribution of the latter to the pattern was too small to be refined and was excluded. No Sn metal was detected. Interestingly a number of unidentified peaks were observed, whose intensity scaled with the SOC during cycling, indicating that they might belong to a new phase formed when charging. No variation in the peak positions was observed excluding the possibility that they
corresponded to a conventional metal hydride battery alloy where the unit cell expands and shrinks with the uptake and release of H. The peaks could be indexed by a small tetragonal unit cell with dimensions a = 3.4049(7) Å and c = 3.255(2) Å. This is similar but still significantly different from a high pressure body centered Sn unit cell of a = 3.70(1) and c = 3.37(1) Å.30 The new tetragonal unit cell is also significantly larger than the cubic body centered cell of a Fe$_{75}$Sn$_{25}$ solid solution with a cell edge of 2.98 Å found previously in a rapidly quenched sample.31 The new tetragonal unit cell is also significantly larger than the cubic body centered cell of a Fe$_{75}$Sn$_{25}$ solid solution with a cell edge of 2.98 Å found previously in a rapidly quenched sample.32 Moreover, C can also be included in the solid solution.33 Interestingly an isostructural solid solution of Sn and Bi can be found at elevated pressures.34 This supports the idea that we have a new solid solution phase composed of some of the elements present in the electrode as all of them have been found to form related structures. A Rietveld refinement assumed a mixed occupancy of Fe, Sn, Bi and C on the (0,0,0) site in a body centered setting did, however, not give a good description of the peak intensities. A good fit was obtained when we reduced the symmetry to P4/mmm with Fe, Sn, Bi and C in (0,0,0) and ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and a D atom in (0,0,0). This is an octahedral interstitial site in the metal atom framework, common for metal hydrides. The additional D position can also be the reason for the deviation from a cubic unit cell. The presence of D makes it difficult to estimate the element ratio in the solid solution. The strong correlation between site occupancy and thermal parameter combined with fairly similar neutron scattering cross sections of the elements in the electrode also aggravates the problem. D and C have almost identical scattering length but the distance to the metal atoms 1.63 Å is more in line with the interstitial atom being D. Hence, the phase was identified as an intermediate hydride phase (IHP). The structure refinement and unit cell parameters of the IHP are given in footnote below. The relative intensity ratio of Fe$_3$O$_4$ to Fe was even at the fully charged state and validated the inactive layer formation that was observed from the SEM and XRD data. Both the nuclear and the magnetic structures were refined using the cubic spinel structure unit cell in space group Fd-3m for the Fe$_3$O$_4$ phase. The magnetic moment was fixed at 4 $\mu_B$ for each of the 8 Fe$^{3+}$ atoms on the tetrahedral site, and $-3.6 \mu_B$ for each of the 16 Fe$^{3+}$ and Fe$^{2+}$ atoms on the octahedral site, and an antiparallel formation was obtained resulting in ferrimagnetic order.30 In the end, good agreement between observed and calculated data was achieved and the model converged with a goodness-of-fit of $\chi^2 = 2.56$ for the pattern shown in Figure 6 (see footnote below for weight fraction refinement results).3

Figure 7a shows the series of neutron diffraction patterns collected over the course of 10 h as the cell was first discharged and then charged (as detailed in Figure 7b). Selected reflections characteristic of individual phases and showing a notable change over time are indicated. Moreover, the phase fractions of all phases were refined for each neutron diffraction pattern. The relative weight fractions of Fe, Fe$_3$O$_4$ and the IHP are shown in Figure 7b. As mentioned in an earlier section, the cell was charged prior to the in situ measurement with fresh electrolyte to ensure that all conductive material was fully reduced. The refilled Sn(OH)$_6^{2-}$ ions were expected to undergo the reduction reaction concurrent with H$_2$ evolution during the initial charge, thus a higher initial weight fraction of the IHP was observed. The specific discharge capacity achieved during cycling was 380 mA g$^{-1}$ similar to the last cycle from the activation of the Fe electrode shown in Figure S4 in the supplementary information. Upon the electrochemical cycling, the intensity of the new set of peaks from the IHP varied with respect to the peaks from the discharged Fe$_3$O$_4$ phase in such a way that we interpreted the hydride to constitute a new phase in the charged state. Initially, the phase evolution of Fe and Fe$_3$O$_4$ was in accordance to the electrochemistry during cycling. The Fe$_3$O$_4$ phase was depleted. The correlation indicated that the metal atom framework of the IHP further constitutes a disordered solid solution of participating Sn, Fe, Bi and C elements. Sn metal was never detected in situ. After completion of the in situ neutron diffraction experiment the Fe electrode, in a fully charged state, was removed from the cell, rinsed, scraped off the Ni mesh and analyzed ex situ by XRD as shown in Figure S5 in the supplementary information. The following phases were observed from the Fe electrode: Fe, Fe$_3$O$_4$, C, Bi and small amounts of Sn. The detection of Sn metal from the XRD pattern indicated that the IHP was metastable and decomposed. The hypothesis on the decomposition of the IHP was corroborated by the in situ phase evolution correlation between C and the IHP, and the observed Sn metal from the ex situ XRD pattern. Thus, the proposed reaction mechanism for the Fe electrode with 0.1 M K$_2$SnO$_3$ during charge was a combined formation of Fe and the IHP. During discharge the products proposed were solid Fe$_3$O$_4$ and dissolved Sn metal formed into Sn(OD)$_6^{2-}$.

Conclusions

In this work we presented the effect of the K$_2$SnO$_3$ to the alkaline Fe electrode by electrochemical and structure characterization. The Fe electrode with the additive exhibited stable charge and discharge cycle performance beyond 150 cycles at 85.3 ± 4.8% coulombic efficiency. The additive extended the first discharge plateau which resulted in an increase of the specific discharge capacity with 60–80 mA h g$^{-1}$. The results presented in this work were promising as it did not need pure or nanostructured Fe powder. Perhaps, with the use of purer and finer Fe powder with the additive, the performance might

| Atom            | x   | y   | z   | Occupancy | $B_{iso}$ (Å$^2$) |
|-----------------|-----|-----|-----|-----------|------------------|
| (Fe$_2$Sn,Bi,C)$_2$D | 0   | 0   | 0   | 1         | 0.0535           |
| (Fe$_2$Sn,Bi,C)  | 1/2 | 1/2 | 1/2 | 1         | 0.0535           |
| D               | 1/2 | 1/2 | 1/2 | 1         | 0.0556           |
| a = b = 3.4049(7) Å, c = 3.255(2) Å, α = β = γ = 90° |
| Volume = 37.74(3) Å$^3$, Space group: P4/n n m m, z = 1 |

$^*$Structure refinement results for (Fe$_2$Sn,Bi,C)$_2$D.

$\chi^2 = 2.56$ for the pattern shown in Figure 6 (see footnote below for weight fraction refinement results).3

$^1$Weight fraction refinement results in Figure 6.
improve significantly, conclusively leading to more active sites upon reducing deposited species. The post-cycled charged Fe electrode with the additive was investigated and confirmed metallic Sn deposition on the surface from EDS, XRD and XPS. Most interesting was the detection of a new phase, IHP, suggested to be a solid solution of the participating metals and maybe also C. The IHP was only detected in situ when no Sn was detectable, while ex situ the IHP decomposed and Sn metal was detected. The combined effect of Fe and the new hydride leads to an increased H2 evolution overpotential and a prolonged discharged state at conventional battery operation. This is beneficial for a practical battery and the more stable discharge voltage of the first discharged state at conventional battery operation. This is beneficial for the close agreement between the potential of Fe and H.

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Figure 7. a) In situ neutron diffraction patterns collected from a cell containing Ni mesh and Fe electrode as positive and negative electrodes, respectively. Each pattern was accumulated over the course of 1 hour. The electrolyte was 6 M KOD and 0.1 M K2SnO3. The evolution of the highlighted reflections and their corresponding phases are shown. b) Plot of the weight fraction (blue, red and black markers with error bars) and the cell potential vs. O2/H2 (dashed green line) as a function of time.