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A Low-Cost Iron-Based Current Collector for Alkaline Battery Electrodes

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The use of three-dimensional porous nickel foam as the current collector of the nickel hydroxide electrode adds significantly to the cost of the nickel-based alkaline rechargeable batteries. Although iron is considerably less expensive than nickel, iron corrodes at the operating potential of the nickel hydroxide electrode. We have found that a 70–100 nm thick thermal coating of cobalt ferrite spinel protects the iron from corrosion. Such a coated iron substrate was found to be stable against corrosion even when polarized anodically at 10 mA cm\(^{-2}\) in 30% potassium hydroxide electrolyte for 1000 h. While the thermal coating of cobalt ferrite protected iron against corrosion, incorporation of lithium ions into the coating was found to enhance the electrical conductivity of the coating. XPS and EXAFS studies confirmed that the enhanced conductivity resulted from an increase in the population of Co\(^{3+}\) in the ferrite spinel lattice. An inexpensive iron (steel) substrate protected by such a coating when used as a nickel hydroxide battery electrode exhibited a specific capacity of 0.25 Ah g\(^{-1}\) at C/5 discharge rate, comparable to a nickel hydroxide electrode based on a relatively expensive nickel foam substrate. The steel-based electrode also exhibited no noticeable degradation over 150 cycles at C/2 rate. This demonstration of a robust and economical steel substrate presents a unique opportunity to reduce the cost of the nickel hydroxide battery electrode in alkaline batteries.

Experimental

Preparation of surface-protected steel substrates.—Mild steel mesh (mesh size 60, wire diameter 0.0075") with an open area of 31% was used as the substrate. To ensure sufficient porosity, the steel mesh was cut and folded into three layers each having a geometric area of 5 cm \(\times\) 5 cm area with a 4 cm long tab on one side for the external electrical connection. Prior to applying the coating, the steel substrate was degreased by ultrasonication for 15 min in isopropanol. Then the cobalt ferrite coating was applied in two steps.

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Step 1: Dipping the substrate in a 0.1 M Co(NO₃)₂ solution in water-isopropanol-acetone mixture (80:10:10 v/v/v) and sonicating for 15 min.
Step 2: Heating the substrate at 400 °C for 30 min in air to form the cobalt ferrite.

For the incorporation of lithium ions, the required amount of lithium nitrate was directly added to the precursor solution in Step 1. The cobalt-ferrite-coated steel and lithium-doped cobalt ferrite coated steel samples have been designated as CS and LCS.

Figure 1. SEM images of the surface of steel substrates after coating with (a) CS, (b) LCS-20, and (c) LCS-50.

Figure 2. (a) Cross sectional TEM image of CS, and elemental maps for (b) cobalt (blue), and (c) iron (green).
respectively, with the percent of lithium doping indicated by a number. For instance, LCS-20 refers to 20% lithium incorporated in the cobalt ferrite coating.

**Preparation of nickel hydroxide battery electrodes.**—An electrode slurry was prepared by mixing of spherical nickel (II) hydroxide (BASF AP-87 Co4), acetylene black, and ethyl cellulose (Ethocel, Standard 45, Dow Chemical Co.) in isopropanol in 80:10:10 (w/w/w) ratio. Ethyl cellulose was first dissolved in isopropanol by sonication to get a 10 wt% solution which was then added to the electrode slurry. Acetylene black was added to enhance the electrical conductivity of the active material mix containing insulating nickel (II) hydroxide active material. The ethyl cellulose served as the binder to connect the active material and carbon particles. After thorough mixing, the electrode slurry was pasted on the surface of the protected steel mesh substrate and dried at 70 °C for 2 h. The coating and drying processes were repeated until the desired loading was achieved. Finally, the electrodes were dried at 70 °C overnight. Typically, the active material loading was 80 mg cm⁻². For comparison, nickel hydroxide electrodes were also prepared on nickel foam (thickness: 2.2 mm, density: 420 g cm⁻³) using the same pasting and curing procedure described above.

**Electrochemical measurements.**—All electrochemical measurements were carried out in a three-electrode polypropylene cell with a mercury/mercuric oxide (MMO) reference electrode (in a 30 wt% potassium hydroxide aqueous solution, E° = 0.098 V vs Normal Hydrogen Electrode, NHE) and nickel-mesh counter electrodes on either side of the working electrode. An aqueous solution of 30 wt% potassium hydroxide solution with 1 wt% lithium hydroxide was used as the electrolyte. We selected this electrolyte composition as it is commonly used in commercial alkaline batteries. The electrochemical stability of the cobalt ferrite coating was tested by anodic polarization at 10 mA cm⁻² for 1000 h. The current density of 10 mA cm⁻² corresponded to a C/2 rate in the battery electrode testing, and the electrode potential during this stability measurement was close to 0.6 V vs NHE which also corresponded to the upper limit of the electrode potential of the nickel battery electrode during charging. To study the response of the coated substrate over the potential range of operation of the nickel hydroxide electrode, we also carried out cyclic voltammetry measurements at a scan rate of 10 mV s⁻¹ over the potential range of 0 to 0.6 V vs MMO. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 10 kHz to 1 Hz with a sinusoidal voltage excitation of 2 mV. Nickel hydroxide battery electrodes were repeatedly charged and discharged at C/5 rate for 20 cycles to achieve as stable capacity, a process referred to as “formation.” To investigate the factors affecting the active material utilization in the battery electrodes, we also performed several experiments on nickel electrodes after formation, by charging and discharging at different rates.

**Characterization of surface structure and composition.**—The surface morphology and elemental composition were studied by scanning electron microscopy (SEM) by placing a cut section of the coated substrate on the sample stub (SEM, JSM-7001 with EDX unit). The phase composition and crystallinity of all the samples were investigated by powder X-ray diffraction (XRD, Rigaku Ultima IV diffractometer, Cu Kα-alpha source). X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD) was used to investigate the surface composition of the coating. All XPS spectra were calibrated against the Cls internal signal at 284.5 eV. Samples for X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) studies were prepared in the same way as for the SEM studies. Morphology, thickness, and elemental distribution of the surface films were probed by transmission electron microscopy (TEM). A sub-100 nm thick cross-section of the coated substrate was prepared using standard focused-ion beam techniques (FEI Nova 600 NanoLab DualBeam) and the resulting lamella was imaged using a TEM (JEOL JEM-2100F) at 200 kV. Cobalt K-edge X-ray Absorption Near Edge Spectroscopy (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) studies were carried out at the Sector 20-BM beamline at the Advanced Photon Source (Argonne National Laboratory). The incident beam was rendered monochromatic using a pair of Si (111) crystals and focused to a spot of ~500 μm diameter at the sample position using a toroidal focusing mirror. The fluorescence signal was monitored using a multi-element, energy dispersive germanium detector. The leading part of the cobalt-K edge signal was selectively windowed to minimize overlap with the iron-K edge background that also emanated from the sample. Harmonic contamination of the incident beam was suppressed using a rhodium-coated harmonic rejection mirror. A reference cobalt foil was simultaneously measured to ensure energy calibration. The threshold energy (defined using the position of the first inflection point) was taken as 7708.8 eV.¹¹ The uncertainty in energy between the various samples is estimated to be ±0.05 eV. Measurements of cobalt oxide/hydroxide standards were also carried out. Data reduction followed standard procedures using established software.¹² The samples for XANES were prepared on large steel foil substrates, and the materials were scraped off using a ceramic blade. The samples were then placed in a thick Teflon frame with kapton tape sealing on either side of the frame.

**Results and Discussion**

**Substrate structure and phase composition.**—The steel mesh substrate after thermal coating of cobalt ferrite (CS) had numerous randomly-oriented nanometer-sized flake-like structures which

![Figure 3](image-url)
appeared to be interconnected to form a dense flake-like structure (Fig. 1a). The interwoven structure created macropores with the size of the pores ranging from 50 to 200 nm. However, we can expect that the bottom section of these individual pores to be covered with cobalt ferrite layer protecting the underlying steel substrate because of reaction of the cobalt nitrate with the iron substrate during coating. In the coating containing 20% lithium (LCS-20), the flake morphology is retained but with larger pores with pore size in the range of 100–300 nm (Fig. 1b). The flakes are also slightly thicker compared to that in the pristine cobalt ferrite coating. Further, the increase of lithium content (LCS-50) does not alter the morphology significantly (Fig. 1c). A similar morphology is reported in the literature for sulfur-doped cobalt ferrite nanoparticles.13

Figure 2 shows the cross-sectional TEM images of CS along with elemental maps. The top-most layer is from the platinum used during the focused-ion beam etching of a thin section of the coating. The dense porous middle layer represents the CS coating. Thickness of this layer ranges from 70 to 100 nm. Figures 2b and 2c suggest uniform distribution of cobalt and iron throughout the coating. The bulk of the material remains as steel without significant conversion from the thermal treatment used for the coating (Fig. 2c). It is anticipated that the growth of the CS layer is self-limiting owing to limited availability of Co$^{2+}$ ions on the surface.

XRD patterns were recorded to identify the phase composition and to probe any change in the lattice parameter resulting from lithium doping. Diffraction peaks at 2-theta values of 45°, 65.1° and 82.3° corresponding to diffraction from (100), (200) and (211) planes of α-iron (Fig. 3a–i) were present in all samples14 suggesting that the bulk of the substrate remained as steel and the thermal coating was limited to a thin layer on the surface, consistent with the TEM results. In the case of CS, additional peaks appeared at 30.5°, 35.7°, 43.4°, 57.1° and 63° (Fig. 3a–ii). These peaks were assigned to (220), (311), (400), (511) and (440) reflections from an FCC phase consistent with the formation of the cobalt ferrite (CoFe$_2$O$_4$) spinel.15 No additional impurity reflections were observed suggesting a phase-pure coating. The spinel phase was retained in the case of LCS-20 (Fig. 3a–iii) and LCS-50 (Fig. 3a–iv). However, the peaks were shifted to higher 2-theta values indicating incorporation of lithium ions into the spinel lattice. This observation was consistent with the literature on lithium-doped cobalt ferrite prepared by the sol-gel combustion method.16 In the present case, Li$^{+}$ (ionic radius 74 pm) could substitute for the larger Co$^{2+}$ ions (ionic radius 82 pm) leading to a net lattice contraction and shift of diffraction peaks to slightly higher 2-theta values (Fig. 3b). Instead, if Li$^{+}$ replaced the smaller Fe$^{3+}$ ions (ionic radius 67 pm), lattice swelling would be expected.17 As discussed in the later sections, the lithium ions play a significant role in increasing the electrical conductivity of the coating.

**Surface composition.**—Surface composition and oxidation state of the metal ions in the thermal coating were examined using XPS and XAS. The photoelectron and Auger peaks in the XPS survey spectrum (Fig. 4a) indicate iron, cobalt, lithium and carbon as the major elements present. Thus, other elemental impurities were below the detectable limit. The resolution of the Co 2p peak allows the assignment of oxidation states of cobalt. In general, pure Co$^{3+}$ compounds show a very weak shake-up peak in the Co 2p spectrum,
whereas pure Co\(^{2+}\) has prominent shake-up peaks that are 4–6 eV higher in binding energy (BE) compared to the main photoelectron signal. If both oxidation states are present, instead of distinct shake-up peaks, a very broad plateau is observed.\(^{18,19}\) As it is shown in Fig. 4b, the deconvolution of higher resolution Co 2p\(_{3/2}\) peak in LCS-20 generates three peaks at 778.5, 779.3 and 780.5 eV which can be assigned to Co\(^{2+}\) in the octahedral sites, Co\(^{3+}\) in tetrahedral sites, and Co\(^{3+}\) in octahedral sites.\(^{20}\) In addition, there is a broad shake-up feature centered around 788 eV similar to that reported in mesoporous Co\(_3\)O\(_4\).\(^{21}\) This peak suggests that the surface coating with lithium doping has mixed oxidation states of +2 and +3 for cobalt. Similarly, deconvolution of the Fe 2p core level spectrum suggests two kinds of lattice sites for Fe ions (Fig. 4c). The doublet of Fe 2p\(_{3/2}\) signal at 709.3 eV and Fe 2p\(_{1/2}\) peak at 722.6 eV is due to Fe\(^{3+}\) in the octahedral sites whereas the doublet of Fe 2p\(_{3/2}\) binding energies at 711.3 eV and Fe 2p\(_{1/2}\) binding energies at 724.4 eV are

![Graphs and diagrams](https://example.com/graphs.png)

Figure 5. Comparison of cobalt in CS-200, CS, and LCS-20 to Co(OH)\(_2\) and Co\(_3\)O\(_4\) standards: (a) Co K-edge XANES, (b) expanded view of the pre-edge peak, (c) \(k^2\)-weighted EXAFS, and corresponding (d) magnitude and (e) real part of the Fourier transform.
due to Fe$^{3+}$ in the tetrahedral sites.$^{22}$ The binding energy spectrum exhibits broad and strong satellite characteristic of high spin Fe$^{2+}$ in the octahedral sites. It is likely that the oxidation of Co$^{3+}$ to Co$^{4+}$ is partially compensated by the reduction of Fe$^{3+}$ to Fe$^{2+}$. The peak at 529.1 eV in the O1s spectrum (Fig. 4d) arises from the metal-oxygen bonding in the cobalt ferrite and the peak at 530.6 eV indicates the presence of metal-hydroxide bonding as in M–OH bond (M = Co(II) or Fe(III)).$^{23}$

Figure 5a shows the XANES of the samples compared with $\beta$-Co(OH)$_2$ and spinel Co$_3$O$_4$ standards. An expanded view of the pre-edge is shown in Fig. 5b. In $\beta$-Co(OH)$_2$, Co is octahedrally coordinated as Co(II)O$_6$. The edge-position of this standard is lowest among the curves displayed in Fig. 5a. Also, due to the presence of a fairly symmetric octahedra, the pre-edge peak at $\sim$7709 eV has relatively small intensity. The XANES of spinel Co$_3$O$_4$ has contribution from both tetrahedral Co(II)O$_4$ and octahedral Co(III)O$_6$. The edge-position is highest among the samples shown in Fig. 5a due to the higher average oxidation state and the pre-edge peak at $\sim$7709 eV has significant intensity due to the presence of tetrahedral Co ions. Further, there is a broad feature at $\sim$7711 eV in the spectra of Co$_3$O$_4$, which is typically attributed to non-local interactions in cobalt oxides.$^{24}$ The pre-edge of CS-200 sample (i.e., CS sample prepared at 200 °C) exhibits slightly enhanced intensity relative to $\beta$-Co(OH)$_2$, but is significantly lower than that seen for Co$_3$O$_4$. This suggests that a majority of the Co in CS-200 is present in octahedral environments, although a minority fraction is tetrahedrally coordinated also. In addition, there is a weak but clear feature at $\sim$7711 eV, similar to that seen for Co$_3$O$_4$. The pre-edge intensity of the CS sample is larger than CS-200 but slightly lower than Co$_3$O$_4$ or LCS-20. The edge shape and position of the CS and LCS-20 samples start resembling Co$_3$O$_4$, with the LCS-20 being most close to Co$_3$O$_4$. The general appearance of the XANES of CS and LCS-20 samples, gradually transitions in shape form that seen for CS-200 to that of Co$_3$O$_4$.

The raw EXAFS $\chi(k)$ spectra and both the amplitude and real part of the corresponding Fourier transforms (FTs) are shown in Figs. 5c–5e. A cursory inspection shows that the major correlations present in Co$_3$O$_4$ are also present in the CS and LCS-20 samples. This is in contrast to the CS-200 sample, which has only some features similar to Co$_3$O$_4$. To help identify potential correlations present in the samples, selected regions are highlighted in real part of the FTs. The Co-O bonds (from both octahedral and tetrahedral Co sites) contribute to the region highlighted in grey. The Co-metal correlations contribute to the region highlighted in red. It is clear that a majority of the cobalt in the CS (and LCS-20) sample has environments similar to Co$_3$O$_4$. However, the amplitude of the correlations does not reach that of Co$_3$O$_4$. In contrast, the features of CS-200 have components that are present both in Co(OH)$_2$ and Co$_3$O$_4$; therefore, the cobalt atoms in CS-200 have environments similar to that seen in both Co(OH)$_2$ and Co$_3$O$_4$. Taken in toto, the XANES and EXAFS observations suggest: (a) the CS-200 sample has cobalt occupying both octahedral and tetrahedral sites. A large fraction of the cobalt is present as Co$^{3+}$ in octahedral sites (akin to Co in Co(OH)$_2$). There is also evidence that a small fraction of cobalt atoms have environments similar to that present in Co$_3$O$_4$, indicating that both Co$^{3+}$ in tetrahedral sites as well as Co$^{3+}$ in octahedral sites are present. Heating treatment at 400 °C converts much of the Co(OH)$_2$ like environments present in CS-200 to a spinel-like environment. The lithium-doped sample has a slightly enhanced spinel-like environment compared to CS and potentially has the least amount of Co$^{2+}$ in Co(OH)$_2$-like, octahedral environments.

**Electrochemical measurements.**—Durability test for the CS substrate.—To be a viable current collector in commercial batteries, the surface-protected steel should exhibit outstanding durability over thousands of hours. To test the robustness of our CS-coated electrode we conducted galvanostatic anodic polarization at 10 mA

![Figure 6](image-url)  
**Figure 6.** Durability test for the CS substrate for 1000 h at 10 mA cm$^{-2}$ in 30% KOH solution.

![Figure 7](image-url)  
**Figure 7.** (a) Formation cycles, and (b) charge and discharge curves at the end of formation for the nickel electrodes on (i) CS substrate and (ii) nickel foam.
cm$^{-2}$ in 30% KOH solution and monitored the electrode potential for 1000 h. The use of a single compartment cell avoided any pH change, and the loss of water was compensated by periodic addition of de-ionized water. Also the reference electrode was checked periodically for any drift in its potential. The extremely low rate of change of potential of 1.5 $\mu$V h$^{-1}$ (Fig. 6a) confirmed that the substrate was stable during the 1000 h of testing. This stability is in sharp contrast to the rapid disintegration and brown coloration of the solution observed when the bare (unprotected) steel mesh was subjected to a similar test.

Formation of nickel hydroxide electrode based on a CS-coated substrate.—The nickel hydroxide electrode using a CS-coated substrate was “formed” by repeated galvanostatic cycling at C/5 charge and discharge rates. During the formation step, utilization of the electrode increases gradually with the number of cycles and reaches a maximum in 20 cycles (Fig. 7a curve (i)). The specific capacity at the end of the 20th cycle was 0.153 Ah g$^{-1}$ which was only 53% of the theoretical capacity. To rule out the possibility that the slurry coating process limited the utilization, we prepared nickel hydroxide electrode on nickel foam using the same slurry coating process, and tested the electrode under identical conditions. The nickel foam-based electrode underwent formation and reached its maximum capacity in 3–4 cycles (Fig. 7a curve (ii)). Furthermore, the end of formation (EOF) capacity was 0.255 Ah g$^{-1}$ (88% of the theoretical capacity), and it was 0.102 Ah g$^{-1}$ higher than that in the case of the nickel electrode on the CS substrate. This undoubtedly indicated that the active material utilization was being limited by the CS substrate. The CS-based electrode also exhibited a higher overpotential compared to the nickel foam electrode during both charge and discharge (Fig. 7b). This higher overpotential was attributed to poor electronic conductivity of the semiconducting CS coating layer compared to metallic nickel (vide infra).

We suspected that the effect of the CS substrate on the utilization of the nickel electrode could be different during charge and discharge. So we studied the utilization of nickel hydroxide electrode using four protocols of charge and discharge at different rates: (i) Charging and discharging at C/5, (ii) charging and discharging at C/50, (iii) charging at C/50 and discharging at C/5, and (iv) charging at C/5 and discharging at C/50. These four types of measurements paved the way to isolate the asymmetric effect of charging and discharging rate on the utilization of active materials. When both charge and discharge rates were C/5, poor utilization close to 0.150 Ah g$^{-1}$ was obtained (Fig. 8a). In contrast, a high utilization of 0.253 Ah g$^{-1}$ was observed when both charge and discharge rates were low at C/50. However, only reducing the charge rate to C/50 while maintaining a high discharge rate at C/5 didn’t result in high specific capacity indicating that the utilization was limited by the poor discharge rate capability. The measurements at low discharge rate (C/50) and high charge rate (C/5) however showed that despite the high rate for charging, specific capacity as high as 0.250 Ah g$^{-1}$ was obtained when discharged at C/50. These four types of measurements proved that the utilization was largely limited by the poor discharge rate capability of the nickel electrode with the CS substrate. Since the CS substrate selectively hindered the discharge process without affecting the charging process, we
hypothesized that the substrate may be existing in two different chemical forms with different electrical conductivity values during charge and discharge of the electrode.

To study the potential-dependent dynamic change in the conductivity of the CS substrate, cyclic voltammograms were recorded for the substrate in the potential window of the nickel hydroxide electrode. As it is seen from Fig. 8b, the CS electrode undergoes oxidative transformation from Co\(^{2+}\) to Co\(^{3+}\) near 0.40 V during the anodic sweep. This peak is reversed and Co\(^{3+}\) reduces back to Co\(^{2+}\) during the cathodic sweep. It is reported that the compounds with cobalt in \(+3\) oxidation state such as CoOOH are electronically more conducting than Co\(^{2+}\) compounds such as Co(OH)\(_2\). Hence it is anticipated that CS substrate will be more conducting at a potential above 0.40 V. Interestingly, the potential during charging of the nickel hydroxide electrode is above 0.40 V whereas the potential during discharge falls below 0.40 V (Fig. 8c). Thus the CS substrate is expected to return to the less conducting Co\(^{2+}\)-rich phase during the discharge process resulting in poor discharge rate capability of the nickel hydroxide electrode based on the CS substrate. Thus, during charge, the substrate existed in a highly conducting Co\(^{3+}\)-rich phase allowing the electrode to be charged at higher rates without any significant reduction of utilization.

**Effect of doping on rate capability.**—We had attributed the lower utilization of the electrodes with the CS substrate to the active change in the electronic conductivity from the Co\(^{2+/3+}\) redox process. Since Co\(^{3+}\) improved the conductivity and favored charging, we hypothesized that substitutional-doping of monovalent ions such as Li\(^+\) for Co\(^{2+}\) in CoFe\(_2\)O\(_4\) would result in increase in the fraction of Co\(^{3+}\) ions in the coating, leading to a stoichiometry of Li\(^+\)\(_x\)Co\(^{2+/3+}\)\(_{1-x}\)Co\(^{3+}\)\(_{1-x}\)Fe\(_2\)O\(_4\), where \(x\) was the level of doping. As is evident from XRD (Fig. 3) addition of LiNO\(_3\) to the Co(NO\(_3\))\(_2\) solution bath during the coating process and subsequent annealing results in Li\(^+\) doping. XPS of Co 2p is consistent with the XANES data on the increase of Co\(^{3+}\) induced by lithium doping in the coating layer (Figs. 4 and 5).

We prepared nickel hydroxide electrodes on steel substrates coated substrates with CS of different lithium doping levels (LCS-10, LCS-20, etc) and compared their performance with electrodes made with just the CS coating. To focus on the effect of lithium doping on the performance, we discharged and charged at high rates of C/5. The nickel hydroxide electrodes prepared with substrates that included lithium as a dopant underwent formation in fewer cycles compared to the electrodes with the undoped substrate (Fig. 9a). The capacity at the end-of-formation (EOF) exceeded 0.22 Ah g\(^{-1}\) for all the electrodes with lithium-doped CS substrates (Fig. 9b). The highest value of EOF capacity was 0.245 Ah g\(^{-1}\) with the 20% Li\(^+\)-doped substrate, close to 0.255 Ah g\(^{-1}\) observed with the nickel foam substrate. The remarkable difference in performance of the nickel hydroxide electrodes using the Li\(^+\)-doped substrates even at high discharge rates confirms the benefit of increased conductivity of the coating resulting from the increase of Co\(^{3+}\) ions in the coating. The benefit is also clear in the low polarization levels observed during charge and discharge curves of the nickel hydroxide electrode when the substrates are coated with the Li\(^+\)-doped spinel (Fig. 9c). Impedance measurements depicted as Nyquist plots in Fig. 9d show
of charging process.\textsuperscript{29} The remaining loss is attributed to the formation of material that cannot be discharged at the same high rates. There was about 7\% of the capacity loss in the first cycle from such material that cannot be discharged at a high rate. However, this fraction was found to increase to 10\% after 150 cycles (Fig. 10b schematics). However, this capacity could be recovered by discharging at a lower rate and was not considered a permanent loss. Since, this fraction of the capacity loss is recovered by discharging at a low current (LCD), it can be considered as a reversible loss. Thus, cycling tests suggested that the nickel hydroxide electrode fabricated with a steel current collector protected by the LCS-20 was stable for at least 150 cycles over a 600-h period of charge and discharge.

Studies on alternate iron-based substrates.—The surface modification protocol developed here is a general strategy for protecting iron based substrates from anodic corrosion in alkali, and not restricted to the steel mesh alone. Specifically, we have found that the thermal coating is feasible with 3D current collectors such as sintered steel wool and iron foam (Figs. 11a and 11b). The sintered steel wool substrate was prepared by treating steel wool (Homax, extra fine grade #0000, 200 g m\textsuperscript{−2}) at 950 °C for 1 h under flowing argon atmosphere. The iron foam (American elements, 99.5\% iron) was used as procured, after degreasing with acetone. These substrates were modified with the spinel coating as in the case of the steel mesh electrodes. The nickel battery electrodes with the surface-protected steel wool and iron foam substrates could be prepared and formed to the capacity of 0.162 Ah g\textsuperscript{−1} and 0.212 Ah g\textsuperscript{−1}, respectively, (Fig. 11c) in much the same way as the steel mesh substrates. While we did not strive to optimize the performance of these electrodes, the results demonstrated the viability of this cobalt spinel-based coating to modifying various types of iron-based porous current collectors that are used in the battery industry.

Conclusions

We have developed a thermal coating to protect iron-based current collectors for the nickel hydroxide battery electrode. The coating protected the iron substrate from corrosion in alkali at the potentials of operation of the nickel hydroxide electrode. The coating was a thin (70–100 nm) cobalt ferrite layer obtained by the thermal decomposition of cobalt nitrate on the surface of steel mesh. The surface-protected steel exhibited outstanding stability for 1000 h at 10 mA cm\textsuperscript{−2} in 30\% potassium hydroxide solution. This level of stability was in sharp contrast to the rapid disintegration observed for bare steel under similar conditions. Although the cobalt ferrite coating was protective, its electrical conductivity needed to be higher to achieve good utilization of the nickel hydroxide electrode. Specifically, the cobalt ferrite coated steel mesh impeded discharge whereas it was able to support high rate charge. We attributed this anomalous phenomenon to the potential dependent variation in the electrical conductivity of the cobalt ferrite owing to Co\textsuperscript{2+}/2\+ redox process around 0.4 V vs MNO that allowed Co\textsuperscript{2+} to be produced during charge but only Co\textsuperscript{2+} to be present upon discharge. We were able to increase the conductivity of the coating during discharge by incorporating Li\textsuperscript{+} ions to cobalt ferrite lattice. XPS and XAS studies confirmed that the conductivity enhancement by lithium doping was due to the increase in the fraction of Co\textsuperscript{2+} in the spinel structure. The nickel hydroxide electrode based on lithium-doped cobalt ferrite coated steel mesh provided specific capacity of 0.25 Ah g\textsuperscript{−1} at C/5 discharge rate which was comparable to the utilization obtained for the nickel-foam-based electrode. The nickel hydroxide electrode based on the surface-modified steel substrate also exhibited good cycle life over 150 cycles at C/2 rates. Development of such a robust and cost-effective surface-protected steel substrate provides a unique opportunity to reduce the cost of positive electrodes in alkaline batteries.
Acknowledgments

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Conflict of Interest Statement

One of the authors, S. R. Narayanan, is a member of the Board of Staq Energy that is engaged in developing nickel-iron batteries.

References

1. J. Chen, D. H. Bradhurst, S. X. Dou, and H. K. Liu, J. Electrochem. Soc., 146, 3606 (1999).
2. S. N. Begum, V. S. Muralidharan, and C. A. Basha, Int. J. Hydrog. Energy, 34, 1548 (2009).
3. P. Periasamy, B. R. Babu, and S. V. Iyer, J. Power Sources, 62, 9 (1996).
4. W. H. Zhu, D. J. Zhang, G. D. Xhang, and J. J. Ke, Mater. Rev. Bull., 30, 1133 (1995).
5. H. Fukunaga, M. Kishimi, N. Igarashi, T. Ozaki, and T. Sakai, J. Electrochem. Soc., 152, A42 (2005).
6. B. Beverskog and I. Puigdomenech, Corros. Sci., 38, 212 (1996).
7. L. Miskova, G. Maurin, M. Monev, and C. Tsveleva, J. Appl. Electrochem., 33, 93 (2003).
8. C. A. Loto, Silicon, 8, 177 (2016).
9. D. Mitra, P. Trinh, S. Mallikdar, M. Mecklenburg, S. M. Heald, M. Balasubramanian, and S. R. Narayanan, J. Electrochem. Soc., 165, F392 (2018).
10. D. Mitra, A. Irshad, S. R. Aravamuthan, and S. R. Narayanan, ECS Meeting Abstracts, MA2018-01, 1691 (2018), http://ma.ecsdl.org/content/MA2018-01/29/1691.abstract.
11. S. Kraft, J. Stümpel, P. Becker, and U. Kuetgens, Rev. Sci. Instrum., 67, 681 (1996).
12. B. Ravel and M. Newville, J. Synchrotron Radiat., 12, 537 (2005).
13. D. Cao, X. Wang, L. Pan, H. Li, P. Jing, J. Wang, and Q. Liu, J. Mater. Chem C, 4, 951 (2016).
14. A. Irshad and N. Murichandraiah, RSC Adv., 7, 21430 (2017).
15. R. H. Kadam, S. T. Alone, M. L. Mane, A. R. Biradar, and S. E. Shirsath, J. Magn. Magn. Mater., 355, 70 (2014).
16. M. K. Shobana, J. Phys. Chem. Solids, 73, 1040 (2012).
17. R. H. Kadam, S. T. Alone, M. L. Mane, A. R. Biradar, and S. E. Shirsath, J. Magn. Magn. Mater., 355, 70 (2014).
18. D. Gu, C. J. Jia, C. Weidenthaler, H. J. Bongard, B. Spliethoff, W. Schmidt, and P. Schult, J. Am. Chem. Soc., 137, 11407 (2015).
19. P. Li, R. Ma, Y. Zhou, Y. Chen, Z. Zhou, G. Liu, Q. Liu, G. Peng, Z. Liang, and J. Wang, J. Mater. Chem. A, 3, 15598 (2015).
20. Z. Zhou, Y. Zhang, Z. Wang, W. Wei, W. Tang, J. Shi, and R. Xiong, Appl. Surf. Sci., 254, 6972 (2008).

Figure 11. Photographs of (a) sintered steel wool, (b) iron foam substrates, approximately 25 cm² in geometric area. (c) capacity of nickel electrode during formation on surface modified (i) sintered steel wool and (ii) iron foam substrates.
21. K. Zhu, C. Jin, Z. Klencsár, A. S. Ganeshraja, and J. Wang, *Catalysts*, 7, 138 (2017).
22. T. Aghavnian, J. B. Moussy, D. Stanescu, R. Belkhou, N. Jedrecy, H. Magnan, P. Ohresser, M. A. Arriod, P. Sainctavit, and A. Barbier, *J. Electron. Spectrosc. Relat. Phenom.*, 202, 16 (2015).
23. J. L. O. Quinonez, U. Pal, and M. S. Villanueva, *ACS Omega*, 3, 14986 (2018).
24. F. Groot1, G. Vanko, and P. Glatzel, *J. Condens. Matter Phys.*, 21, 104207 (2009).
25. V. Pralong, A. D. Vidal, B. Beaudoin, J. B. Leriche, and J. M. Tarascon, *J. Electrochem. Soc.*, 147, 1306 (2000).
26. P. Oliva, J. Leonardi, J. F. Laurent, C. Delmas, J. J. Bracconnier, M. Figlarz, F. Fievet, and A. deGuibert, *J. Power Sources*, 8, 229 (1982).
27. K. H. Young and S. Yasuoka, *Batteries*, 2, 3 (2016).
28. J. Chen, D. H. Bradhurst, S. X. Dou, and H. K. Liu, *J. Mater. Res.*, 14, 1916 (1999).
29. D. A. Corrigan, *J. Electrochem. Soc.*, 134, 377 (1987).