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Elucidating the Impact of Cobalt-Doping on the Lithium Storage Mechanism in Conversion/Alloying-type Zinc Oxide Anodes

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Abstract

Herein, an in-depth investigation on the influence of transition metal doping on the structural and electrochemical characteristics of a hybrid conversion/alloying-type lithium-ion anode material is presented. Therefore, pure zinc oxide (ZnO) and cobalt-doped ZnO (Zn$_{0.9}$Co$_{0.1}$O) were comparatively investigated. The characterization by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) confirmed the successful incorporation of the cobalt (Co) dopant into the wurtzite ZnO structure, leading to a decreased particle size for the doped compound. The electrochemical in situ XRD analysis of the first de-/lithiation of ZnO and Zn$_{0.9}$Co$_{0.1}$O revealed the highly beneficial impact of the transition metal doping on the reversible degradation of lithium oxide (Li$_2$O) and suppression of the zinc crystallite growth upon lithiation; both effects being essential for the greatly improved electrochemical performance. As a result, the Co-doping lead to a substantially increased specific capacity from 326 mAh g$^{-1}$ for pure ZnO to 789 mAh g$^{-1}$ for Zn$_{0.9}$Co$_{0.1}$O after 75 full dis-/charge cycles.

Keywords: zinc oxide nanoparticles, cobalt doping, conversion/alloying, lithium-ion anode, battery

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1. Introduction

Despite great technological interest in nanostructured zinc oxide (ZnO) for a large variety of applications, including, for instance, light-emitting diodes,[1] gas sensors,[2] or dye-sensitized solar cells,[3] their investigation as lithium-ion anode materials was reported rather scarcely so far. In fact, although a theoretical specific capacity of about 988 mAh g⁻¹ (considering the reaction ZnO + 3 Li⁺ + 3 e⁻ ↔ LiZn + Li₂O as fully reversible) certainly arouses interest, apart from a few outstanding exceptions[4] most electrochemical studies revealed poor performance and rapid capacity fading.[5] In order to explain the origin of this inferior electrochemical performance of ZnO-based electrodes, Pelliccione and co-workers[6] performed very recently an in situ X-ray absorption fine structure (XAFS) spectroscopy study. It was found that this substantial capacity decay mainly originates from the formation of relatively large metallic zinc particles upon continuous de-/lithiation. Once their size exceeds a certain limit, the formation of ZnO accompanied by the degradation of Li₂O, i.e., the conversion reaction, shows no reversibility anymore and only the alloying reaction of zinc with lithium takes place reversibly – which, in turn, is associated with the characteristic issues of alloying materials.[5f]

Also, the large volume changes upon alloying-dealloying lead to the pulverization of the active material, ongoing electrolyte decomposition, and finally the loss of electrical contact within the composite electrode.[5f] Additionally, the decrease in electronic conductivity within the electrode owing to the insulating nature of Li₂O presumably contributes to the observed rapid capacity fading.[6] We have recently reported that these challenges and in particular the reversibility of the conversion reaction can be substantially enhanced by introducing a transition metal dopant into the metal oxide structure.[7] This new concept follows the general approach of introducing a metallic element that does not alloy with lithium once reduced to the metallic state,[8] thus, ensuring a sufficient electron supply throughout the initial particles to enable the degradation of Li₂O. However, little is known so far about the detailed reaction mechanism of this new class of conversion/alloying materials.

In this study, we present an in-depth structural and electrochemical characterization of pure ZnO and Co-doped ZnO nanoparticles, employing XRD, SEM, TEM, cyclic voltammetry (CV), and galvanostatic cycling. Moreover, we performed a comparative in situ XRD analysis of Co-doped and pure ZnO nanoparticles. The obtained results, discussed also in regard to our previous findings for Fe-doped ZnO,[7a]
provide an enhanced understanding of the advantageous impact of the transition metal dopant on the reversibility of the de-/lithiation mechanism in general and the conversion reaction in particular. In fact, doping ZnO with cobalt results in a substantially enhanced specific capacity and cycling stability of nanoparticulate ZnO-based lithium-ion anodes.

2. Experimental Section

2.1 Materials Synthesis

For the synthesis of Co-doped ZnO nanoparticles stoichiometric amounts of zinc (II) gluconate hydrate and cobalt (II) gluconate hydrate (both from ABCR) were dissolved in deionized water. The resulting solution, having a total metal ion concentration of 0.2M, was added dropwise under vigorous stirring to an aqueous 1.2M solution of sucrose (ACROS ORGANICS). After continuous stirring for additional 15 min at room temperature, the solution was heated up to about 160 °C to remove the water. Concurrently, the sucrose started to be thermally decomposed. The remaining solid precursor was further dried at around 300 °C, afterwards ground and calcined for 4 h under air at 400 °C (heating rate: 3 °C min⁻¹). Pure ZnO nanoparticles were prepared following an analogous synthesis protocol in absence of the Co precursor and applying an annealing temperature of 450 °C.

2.2 Morphological and Structural Characterization

Powder X-ray diffraction (XRD) patterns were recorded with a BRUKER D8 Advance employing a Cu-Kα₁ radiation (λ = 154 pm) and setting the step size to 0.0092°. Scanning electron microscopy (SEM) was carried out using a ZEISS LEO 1550VP field emission electron microscope. All samples were sputtered with platinum to prevent charging effects. High-resolution transmission electron microscopy (HRTEM) of Zn₀.₉Co₀.₁O nanoparticles was performed on samples deposited on a copper grid coated by a holey carbon film utilizing a Philips CM 20 at 200 kV.

2.3 Electrochemical Characterization

Electrodes were prepared by dissolving sodium carboxymethyl cellulose (CMC, WALOCEL™ CRT 2000 PPA 12, Dow Wolff Cellulosics) in deionized water (1.25 wt.% of CMC in solution). The
conductive carbon (Super C65®, IMERYS Graphite and Carbon) and ZnO or Zn$_{0.9}$Co$_{0.1}$O nanoparticles were added, resulting in a relative dry material composition of 75 wt.% active material, 20 wt.% conductive carbon, and 5 wt.% CMC. Dispersion of the obtained mixture was carried out by means of planetary ball-milling for 2 h. The resulting slurry was cast on dendritic copper foil (SCHLENK, 99.9%), serving as current collector, utilizing a laboratory doctor blade (wet film thickness: 120 μm). After an initial drying at room temperature overnight, disk electrodes (φ = 12 mm) were punched and vacuum-dried for 24 h at 120 °C. The average active material mass loading was around 2.0-2.5 mg cm$^{-2}$.

The electrochemical characterization was performed in three-electrode Swagelok™-type cells, assembled in an MBraun MB-200B eco glove box (O$_2$ and H$_2$O content < 0.1 ppm), using lithium metal foil (Rockwood Lithium, battery grade) as counter and reference electrodes. The electrodes were separated by a stack of polypropylene fleeces (Freudenberg FS 2190), drenched with a 1M solution of LiPF$_6$ in a 3:7 wt/wt mixture of ethylene carbonate and diethyl carbonate (UBE). As metallic lithium foil was used as counter and reference electrodes, all potential values given herein refer to the Li/Li$^+$ redox couple. Cyclic voltammetry and galvanostatic cycling were performed using a VMP3 potentiostat (BioLogic) and a Maccor Battery Tester 4300, respectively. All electrochemical studies were conducted at 20 °C ± 2 °C in a potential range from 0.01 to 3.0 V.

2.4 In situ XRD Analysis

In situ XRD analysis of Co-doped and pure ZnO nanoparticles upon galvanostatic de-/lithiation was conducted using a self-designed two-electrode in situ cell.$^9$ Electrodes were prepared analogously to those used for the electrochemical characterization, having an overall composition of 65 wt.% active material, 25 wt.% conductive carbon, and 10 wt.% CMC. The resulting mixture was dispersed by means of planetary ball-milling and cast onto a beryllium (Be) disk (thickness: 250 μ, Brush Wellman), serving concurrently as current collector and “window” for the X-ray beam. The coated Be disk was dried for 30 minutes at 80 °C under ambient atmosphere and subsequently at 40 °C under vacuum overnight. Metallic lithium foil served as counter electrode. Two sheets of Whatman glass fiber, drenched with 500 μl of a 1M solution of LiPF$_6$ in a 3:7 wt/wt mixture of ethylene carbonate and diethyl carbonate (UBE), were used as separator. The readily assembled cell was allowed to rest for 10 h prior to the in situ
XRD measurements. Simultaneous galvanostatic cycling was performed by means of a VSP potentiostat/galvanostat (BioLogic), applying a specific current of around 55 mA g\(^{-1}\) (Zn\(_{0.9}\)Co\(_{0.1}\)O) or 60 mA g\(^{-1}\) (ZnO) and setting the cut-off potentials to 0.01 V and 3.0 V. The XRD analysis was carried out in a 2\(\theta\) range from 25 to 80° with a step size of 0.02758° and a time per step of 0.65 s. Consequently, every scan lasted exactly 30 min, including an initial rest step of 419 s.

3. Results and Discussion

3.1 Structural and Morphological Characterization

The X-ray diffraction patterns of pure ZnO and Zn\(_{0.9}\)Co\(_{0.1}\)O, presented in Figure 1, show the characteristic pattern of hexagonal wurtzite structured ZnO with the \(P6_{3}mc\) space group (JCPDS File Card No. 01-071-6424), indicating the synthesis of phase-pure materials and the successful doping of ZnO with cobalt. The additional low intensity reflections at about 28.7°, 31.1°, and 32.7° (marked by asterisks) originate from the diffraction of the Cu-K\(\beta_1\) radiation at the (100), (002), and (101) lattice planes. The Co-doped sample reveals slightly broader full width at half maximum values and lower reflection intensities compared to the pure ZnO, which indicates a reduced crystallite size. These results are in excellent agreement with a recent in-depth crystallographic analysis, reported by Giuliani et al.\(^{[10]}\)

![Figure 1. XRD patterns of as-synthesized ZnO nanoparticles (upper pattern in black) and Co-doped ZnO nanoparticles (lower pattern in green); the JCPDS reference file card no. 01-071-6424 (wurtzite structure, hexagonal symmetry, \(P6_{3}mc\) space group) is given below.](image)
Figure 2 shows the SEM images of the pristine powdery samples. The SEM image of ZnO (Figure 2a) reveals a particle diameter of about 40 nm, while the introduction of Co into the ZnO lattice results in a decreased particle size of around 20 to 30 nm. These findings are in good agreement with the XRD analysis and previous studies.\cite{7a, 10} The TEM micrographs of Co-doped ZnO depicted in Figure 3 confirm this particle size, while revealing the additional presence of slightly smaller (~10 nm) and larger (~35 nm) particles. Moreover, the HRTEM micrograph presented in Figure 3b does not show any significant lattice distortion, further confirming the successful incorporation of the cobalt dopant in the wurtzite ZnO structure.

![SEM micrographs of (a) pure ZnO and (b) Co-doped ZnO nanoparticles at a magnification of 100 kx.](image_url)

![TEM micrographs of Co-doped ZnO nanoparticles at different magnifications.](image_url)
3.2 Cyclic Voltammetry

In Figure 4 the cyclic voltammograms of ZnO- and Zn_{0.9}Co_{0.1}O-based electrodes, studied between 0.01 and 3.0 V, are presented. In the first cathodic sweep, ZnO (Figure 4a) reveals three reduction peaks at potentials of (a) 0.70 V, (b) 0.38 V, and (c) 0.13 V. Subsequently, i.e., below 0.07 V, a continuously decreasing specific current was recorded, which is assigned to charge accumulation at the surface and in the carbon black, employed as conductive additive. Peak (a) at 0.70 V is commonly ascribed to the reduction of electrolyte components at the anode/electrolyte interface resulting in the formation of the solid electrolyte interphase (SEI).\textsuperscript{[11]} The main peak (b) at 0.38 V is mainly related to the reduction of ZnO to form metallic Zn and Li_2O. Subsequently, at potentials below 0.2 V, the metallic Zn alloys with Li. However, the slope of the baseline is rather steep suggesting that the lithiation processes might partially overlap. Upon delithiation various peaks in region (d) at 0.19 V, 0.29 V, 0.35 V, 0.54 V, and 0.68 V, one broad peak (e) at 1.32 V, probably consisting of two overlapping peaks, and a low-intensity peak (f) at 2.55 V were detected. The peaks in the low potential region, i.e., below 0.75 V, are related to the stepwise de-alloying of LiZn as previously reported in literature.\textsuperscript{[5c, 12]} The underlying reaction corresponding to the broad, anodic peak (e) at about 1.32 V remained unexplained for a long time.\textsuperscript{[5c]} Huang \textit{et al}.\textsuperscript{[13]} recently ascribed this feature to the de-alloying of Li_{x}Zn. Moreover, they correlated the low-intensity peak (f) at 2.55 V to the partially reversible degradation of Li_2O accompanied by the formation of ZnO.\textsuperscript{[13]} Nevertheless, considering studies on tin (oxide)-based anodes, it appears also conceivable to assign peak (e) to the partially reversible formation of Li_2O\textsuperscript{[7b]} and peak (f) to a partial degradation of SEI components,\textsuperscript{[14]} in particular, with respect to its absence in case of carbon-coated ZnO.\textsuperscript{[15]} However, we will discuss this assignment of the peaks to specific electrochemical reactions in more detail in consideration of the \textit{in situ} XRD analysis, presented hereafter. During the following sweeps, shown in Figure 4b, new cathodic peaks at (g) 0.96 V and (h) 0.78 V arise, whereas the anodic peak (f) at 2.55 V completely vanishes; the latter is, in fact, in good agreement with the aforementioned studies on tin-based anodes, which assigned this peak to a partial SEI degradation. In addition, the peaks (g), (h), (b), (c), and (e) show a shift towards slightly lower potentials and a considerable intensity decrease. Peak (g) completely disappears after a few cycles. Moreover, peak (b) is split into two peaks, which are assigned to the alloying reaction of Zn with Li, thus, the stepwise alloying becomes more apparent. In contrast, the
peaks in region (d) related to the dealloying processes remain rather unchanged, although revealing a slightly decreasing intensity. In fact, these results evince the often-reported irreversibility of the Li$_2$O degradation and the limited reversibility of the Li-alloying process of Zn.$^{[5a-e, 6]}$

Figure 4. Cyclic voltammograms of ZnO ((a) first sweep, (b) 2$^{nd}$ to 10$^{th}$ sweep) and Zn$_{0.9}$Co$_{0.1}$O ((c) first sweep, (d) 2$^{nd}$ to 10$^{th}$ sweep). Sweep rate: 50 $\mu$V s$^{-1}$; reversing potentials: 0.01 V and 3.0 V vs. Li/Li$^+$.  

In Figure 4c, the first potentiodynamic cyclic sweep for Zn$_{0.9}$Co$_{0.1}$O is presented. Co-doped ZnO exhibits similar characteristics as the undoped ZnO. However, the features are much less pronounced, which might be assigned to the smaller particle and crystallite size as revealed by SEM (Figure 2) and XRD (Figure 1), and slightly shifted to higher potentials, presumably resulting from an enhanced electronic conductivity.$^{[16]}$ Analogous to ZnO, as described above, the SEI formation occurs at about 0.72 V (peak (a)), followed by the reduction of ZnO at (b) 0.46 V. Below 0.25 V the electrochemical alloying of Zn with Li, lithium insertion into the conductive carbon, and charge storage at the surface take
place. According to the standard redox potential, Co is nobler than Zn, i.e., Co is reduced at higher potentials. However, no clear feature, related to the reduction of Co, was observed by performing CV - which is expected considering previous results for zinc and cobalt ferrite.[17] Nonetheless, the influence of the Co-dopant is indicated by a slightly higher potential of peak (a) compared to pure ZnO. During the anodic sweep, the de-alloying of Zn occurs in the potential range between (d) 0.16 V and 0.74 V, followed by the degradation of Li$_2$O (e) at 1.35 V, as mentioned before. In the subsequent cycles, the peaks (a) and (b) vanish and new features (g) at 0.93 V and (h) at 0.81 V appear (Figure 4d). Upon further cycling, the peak intensities of these new features decrease and their maxima are shifted to slightly lower potentials. Additionally, a broad feature characterized by a constantly increasing specific current at a potential of about 0.5 V arises. Nonetheless, compared to ZnO, Zn$_{0.9}$Co$_{0.1}$O shows a remarkably improved reversibility, in particular for peak (e).

3.3 In Situ XRD

In order to further study the structural changes and phase transitions occurring during the electrochemical lithiation and subsequent delithiation reaction and to investigate the influence of the cobalt dopant, in situ XRD analysis was performed on electrodes based on pure ZnO and Co-doped ZnO nanoparticles. In both cases, the electrodes were subjected to a constant current lithiation (discharge) from OCV to 0.01 V and, subsequently, delithiation (charge) from 0.01 V to 3.0 V. The results for the pure ZnO nanoparticles are presented in Figure 5. Figure 5a shows the corresponding potential profile, which can be roughly divided in five different regions (A, B, and C for the discharge as well as D and E for the subsequent charge). To provide an overview on the evolution of the simultaneously recorded XRD patterns, a waterfall diagram showing all XRD patterns is presented in Figure 5b, within which these regions are indicated by the scans highlighted in red. A detailed discussion of the therein-occurring processes, however, is based on the following panels. Region A covers the initial potential decrease until the onset of the voltage plateau at about 0.55 V. For this region (scans 1-5), a decrease in intensity of the main wurtzite-related reflections is observed (Figure 5c; marked by the black arrows), indicating an incipient reduction of the long-range order within the wurtzite structure. This structural change is accompanied by some electrolyte decomposition, indicated by the slight change in slope of the discharge
curve, which is in good agreement with the CV results (Figure 4a). The initial reduction of the oxide is -
though somehow expected - of particular interest, as it is in contrast to our earlier finding for Fe-doped
ZnO,\textsuperscript{7a} for which we did not observe any initial decrease in intensity during the first scans. In fact, this
remarkable difference regarding the structural evolution may support our previous assumption that for Fe-
doped ZnO prior to the onset of the voltage plateau an insertion of lithium ions into the wurtzite structure
may occur, favored by the presence of cationic vacancies in Zn\textsubscript{0.9}Fe\textsubscript{0.1}O as proposed by Giuli \textit{et al.}\textsuperscript{[10]}
A careful analysis of the different XRD patterns reveals also the appearance of a very broad and yet tiny
reflection at about 43.0° (marked by the red arrow). Considering the indicated reduction of ZnO
accompanied by the formation of amorphous Li\textsubscript{2}O\textsuperscript{[5e, 6-7, 18]} it appears reasonable to assign this feature to
the main reflection of metallic zinc (JCPDS Card File No. 00-004-0831), which is also in good agreement
with the onset of the following voltage plateau (Figure 5a) assigned to the occurrence of an equilibrium
between different, but simultaneously present phases.

Indeed, for the following scans (Figure 5d, Region B, scans 6-12), the continuous decrease and
increase in intensity of the reflections corresponding to ZnO and Zn\textsuperscript{0}, respectively, indicates that the oxide
is further reduced and more metallic zinc is formed. Starting from scan 13/14, three new reflections appear
at about 37.0°, 41.0°, and 42.7° in the selected 2θ range; the latter one is initially present as shoulder of the
Zn\textsuperscript{0}-related reflection and subsequently continuously increasing in intensity, while the Zn\textsuperscript{0}-related
reflection itself vanishes simultaneously. Their positions and relative intensity are in very good agreement
with the JCPDS Card File No. 01-071-9525 reported for Li\textsubscript{0.105}Zn\textsubscript{0.895}, indicating that along the voltage
plateau the previously formed metallic zinc also starts to alloy electrochemically with lithium, thus,
forming a Li\textsubscript{x}Zn alloy phase with a rather low lithium content, i.e., x << 1. In fact, this finding is further
supported by the concurrent appearance of two additional reflections at around 56.5° and 67.0° - see
Figure 5b. Apparently, the reduction of the oxide and the initial alloying reaction occur partially
simultaneously, i.e., at the same voltage. At the end of the voltage plateau, in scan 19, the reflections
corresponding to the wurtzite-structured oxide completely vanished and only the Li\textsubscript{x}Zn-related reflections
remain.
Figure 5. **In situ XRD analysis of ZnO**: (a) Galvanostatic dis-/charge profile of the first cycle, (b) corresponding XRD patterns, (c) to (g) close-ups of selected XRD patterns.

In Region C, no significant changes are observed for the scans 19-22, i.e., along the initial rather steep voltage decrease. Subsequently, however, the intensity of the two reflections at about 37.0° and 42.7° corresponding to the Li\textsubscript{x}Zn (x ≪ 1) phase decrease in intensity, while the one at around 41.0° continuously increases, initially shifting to slightly larger 2θ values and then back to slightly lower 2θ values. Indeed, analyzing also the extended 2θ range (up to 80.0°) reveals that this shifting and increase in intensity is related to the appearance of the fully lithiated LiZn alloy phase, as, starting from scan 23, also at around 48.5°, 60.0°, and 75.0° new reflections appear. This is in excellent agreement with JCPDS Card...
File No. 03-065-3016 reported for LiZn. In addition, the further lithiation, i.e., the formation of the fully lithiated binary LiZn alloy at potentials below 0.2 V along a sloped voltage plateau is in good agreement with previous, purely electrochemical studies on the lithium-zinc alloying reaction mechanism.\textsuperscript{[5e, 12, 19]}

Finally, in scan 28, only reflections corresponding to the LiZn phase are present, indicating that the lithiation reaction is completed at the end of the discharge step (0.01 V).

For the subsequent charge (scans 29-44), the LiZn-related reflections are first slightly shifted to larger 2θ values, indicating that the lattice parameters slightly decrease, presumably due to a decreasing lithium content in the alloy (Figure 5f, scans 29-32, first slope). Beginning from scan 33 (i.e., after the change in slope), the reflections corresponding to the Li\textsubscript{x}Zn (x \ll 1) phase reappear and steadily increase in intensity, while the reflections related to the LiZn phase keep decreasing. In scan 35, at the end of Region D only the reflections corresponding to the Li\textsubscript{x}Zn phase remain. These reflections, however, abruptly vanish for the next scan (scan 36) as shown in Figure 5g (Region E), in which scan 35 is included again for the sake of clarity. Instead, four new reflections are observed at about 36.2°, 38.8°, 43.0°, and 54.0°, which are in very good agreement with the JCPDS reference reported for metallic zinc (Card File No. 00-004-0831), indicating that the dealloying reaction is completed at around 0.7 V upon charge. This finding is, in fact, also in good agreement with the recorded specific capacity (Figure 5a), as the alloying contribution for ZnO theoretically corresponds to 329 mAh g\textsuperscript{-1}, and our assignment of the different peaks in the CV profile (Figure 4a and b). The subsequent decrease in intensity observed for the two reflections at around 38.8° and 43.0° may be ascribed to the partial re-oxidation of the metallic zinc at potentials higher than 0.7 V.\textsuperscript{[6]} This is further supported by the appearance of a very broad reflection in the range from 31.0° to 35.0° as well as the limited decrease in intensity of the reflection at about 36.2°, as it overlaps with the main reflection of the wurtzite-structured oxide. Nevertheless, this re-oxidation process appears to be limited (see also Figure 4b), as very intense reflections corresponding to metallic zinc remain even at the end of the charge process at 3.0 V. Additionally, the specific capacity obtained in this voltage range is substantially lower than theoretically expected, considering the fully reversible conversion of Li\textsubscript{2}O (ca. 416 mAh g\textsuperscript{-1} rather than 658 mAh g\textsuperscript{-1}). Based on the above-described findings, we may qualitatively describe the multistep process as follows:
(A) \[ \text{ZnO} + \text{Li}^+ + e^- \rightarrow \text{ZnO} + \text{Li}_2\text{O} + \text{Zn}^0 \]

(B) \[ \text{ZnO} + \text{Zn}^0 + \text{Li}^+ + e^- \rightarrow \text{Li}_x\text{Zn} + \text{Li}_2\text{O} \]

(C) \[ \text{Li}_x\text{Zn} + (1-x) \text{Li}^+ + (1-x) e^- \rightarrow \text{LiZn} \]

(D) \[ \text{LiZn} \rightarrow \text{Li}_x\text{Zn} + (1-x) \text{Li}^+ + (1-x) e^- \rightarrow \text{Zn}^0 + \text{Li}^+ + e^- \]

(E) \[ \text{Zn}^0 + \text{Li}_2\text{O} \rightarrow \text{Zn}^0 + \text{ZnO} + \text{Li}^+ + e^- \]

In sum:

\[ \text{ZnO} + 3 \text{Li}^+ + 3 e^- \rightarrow \text{LiZn} + \text{Li}_2\text{O} \quad (\pm 988 \text{ mAh g}^{-1}) \]

Please note that the equations for the single regions are not balanced stoichiometrically as an adjustment by unknown general variables would certainly only complicate the understanding and reading substantially, while not adding any beneficial further information. Also, the electrode chemistry presented for each step focuses only on the reactions taking place in the corresponding potential range. We may note at this point that our findings obtained by performing \textit{in situ} XRD are in excellent agreement with the very recent \textit{in situ} XAFS study by Pelliccione \textit{et al.},\textsuperscript{[6]} who also observed a fully reversible LiZn formation in the first cycle, but the incompleteness of the subsequent re-oxidation of metallic zinc upon delithiation, presumably related to the formation of relatively large metallic zinc particles (approximately 10-20 nm) and the corresponding extensive structural reorganization in the electrode, which was further supported by a very recent \textit{in situ} TEM study.\textsuperscript{[18]}

To investigate the effect of introducing the cobalt dopant in the wurtzite structure, we carried out an \textit{in situ} XRD analysis for Zn\textsubscript{0.9}Co\textsubscript{0.1}O-based electrodes as well (Figure 6). The corresponding potential profile is presented in Figure 6a while the overview on the evolution of the recorded XRD patterns is given in Figure 6b.
Figure 6. **In situ XRD analysis of Zn_{0.9}Co_{0.1}O:** (a) Galvanostatic dis-/charge profile of the first cycle, (b) the corresponding XRD patterns, (c) to (g) close-ups of selected XRD patterns.

Again, the potential profile can be subdivided in five different regions (indicated by the red highlighted scans), following a similar approach as for ZnO. While the larger number of scans is also a result of the slightly lower specific current applied (55 mA g\(^{-1}\) vs. 60 mA g\(^{-1}\) for ZnO), two major differences are evident. The potential profile is generally smoother, i.e., it shows less remarkable changes in slope, which may originate partially from the smaller initial crystallite size\(^{16a, 16b}\) and is in good agreement with the cyclic voltammetry results shown in Figure 4 as well as the slightly higher potential of the main voltage plateau upon discharge. The latter may be assigned to the higher reduction potential of cobalt compared to
zinc. Nevertheless, for the initial reaction of the oxide upon lithiation (Figure 6c, Region A), the same structural evolution is observed: A decrease in intensity of the oxide-related reflections, indicating that also in the case of Co-doped ZnO the oxide is immediately reduced and that no substantial initial lithium ion insertion into the wurtzite lattice takes place. This finding is, again, in good agreement with the in-depth structural analysis by Giuli et al.,\(^{[10]}\) revealing that, in contrast to iron, cobalt is purely divalent, thus, not requiring the presence of, e.g., cationic vacancies to balance trivalent cations in the oxide lattice. In addition, starting from scan 6, i.e., at the onset of the subsequent voltage plateau the appearance of a very broad yet tiny reflection in the range from 41.0° to 45.0° is observed. Its intensity is further increasing during the following scans (Figure 6d, Region B), while the oxide-related reflections are continuously decreasing until they completely vanish at the end of the voltage plateau (scan 22). Remarkably, however, in contrast to ZnO, no well pronounced reflections are observed for the newly appearing reflection in the range from 41.0° to 45.0° and the intensity remains substantially lower in general. In fact, it appears that this rather broad new feature may be composed of two reflections, presumably corresponding to the concurrent formation of metallic Zn\(^{0}\) and Li\(_x\)Zn (at around 43.0° and 42.0°, respectively), which largely overlap. These findings provide two important information: First, the crystallinity of the formed phases is substantially lower than in case of ZnO (similarly to the findings for Fe-doped ZnO\(^{[7a]}\)), indicating – apart from the slightly smaller crystallite size of the pristine oxides (see Figure 2) - the presence of cobalt as dopant prevents the formation of large crystalline particles upon lithiation, i.e., favors the nanocrystallinity of the sample. Second, the introduction of the cobalt dopant appears to kinetically favor the formation of the Li\(_x\)Zn alloy. These two findings are, in fact, of particular interest, as Su et al.\(^{[21]}\) very recently reported that the growth of Zn particles and the alloying reaction are two competing processes, depending on the applied current density. We may thus assume that the formation of a continuous percolating network of metallic cobalt leads to an enhanced electron transport and distribution within the initial nanoparticles, favoring the alloying reaction rather than the zinc crystal growth.

Upon further lithiation (Figure 6e, Region C), beginning from scan 31, a new reflection appears at about 41.0°, which is in excellent agreement with the results obtained for ZnO, indicating the formation of the LiZn alloy phase at a potential of less than 0.2 V (see also Figure 6a).
This reaction is subsequently reversed upon delithiation (i.e., charge; Figure 6f, Region D), just like for ZnO. Nevertheless, the dealloying reaction is apparently completed at relatively higher potentials (ca. 1.2 V compared to about 0.7 V for ZnO; see Figure 5a and Figure 6a, respectively). Also, it appears that for Zn_{0.9}Co_{0.1}O in Region E (Figure 6g) some Li_{x}Zn (x << 1) phase remains, as indicated by the shoulder of the reflection at about 43.0°; the latter assigned to the presence of metallic zinc, though the rather broad nature of the reflection makes it difficult to clearly differentiate between the two phases. This is especially true as no significant additional reflections are observed for this sample. In either case, this rather broad reflection continuously decreases in intensity upon further delithiation until it completely vanishes at the end of the charge process at 3.0 V. Concurrently, a new broad reflection appears within 30.0-37.0° and steadily increases, accompanied by the appearance of an even broader reflection at around 57.0°. Considering the substantially reduced crystallinity of the sample after the first cycle, due to the extensive structural reorganization processes that occur, it appears conceivable that these two broad reflections indicate the reappearance of a wurtzite-structured oxide phase. Moreover, the complete disappearance of the metallic zinc phase in combination with the obtained specific capacity of 970 mAh g⁻¹, i.e., roughly the theoretical capacity expected for the fully reversible formation of LiZn and Li₂O (± 962 mAh g⁻¹), further support the formation of a metal oxide phase at the end of charge - including both zinc and/or cobalt. The slight excess in capacity may be well explained by the lithium storage capability of the comprised conductive carbon, as also observed previously. Based on these results, we propose the following multistep process for the first lithiation and delithiation process:

(A) \( \text{Zn}_{0.9}\text{Co}_{0.1}\text{O} + \text{Li}^+ + \text{e}^- \rightarrow \text{Zn}_{0.9}\text{Co}_{0.1}\text{O} + \text{Co}^0 + \text{Zn}^0 + \text{Li}_2\text{O} \)

(B) \( \text{Zn}_{0.9}\text{Co}_{0.1}\text{O} + \text{Zn}^0 + \text{Li}^+ + \text{e}^- \rightarrow \text{Li}_{x}\text{Zn} + \text{Co}^0 + \text{Zn}^0 + \text{Li}_2\text{O} \) \( (x << 1) \)

(C) \( \text{Li}_{x}\text{Zn} + \text{Zn}^0 + \text{Li}^+ + \text{e}^- \rightarrow \text{LiZn} \)

(D) \( \text{LiZn} \rightarrow \text{Li}_{x}\text{Zn} + \text{Zn}^0 + \text{Li}^+ + \text{e}^- \)

(E) \( \text{Li}_{x}\text{Zn} + \text{Zn}^0 + \text{Co}^0 + \text{Li}_2\text{O} \rightarrow \text{Zn}_{1.3}\text{Co}_y\text{O}^* + \text{Li}^+ + \text{e}^- \) \( (y \approx 0.1) \)
In sum:

\[
\text{Zn}_{0.9}\text{Co}_{0.1}\text{O} + 2.9 \text{Li}^+ + 2.9 \text{e}^- \rightleftharpoons 0.9 \text{LiZn} + \text{Co}^0 + \text{Li}_2\text{O} \quad (\approx 962 \text{mAh g}^{-1})
\]

Please note that also in this case, the equations for the single regions are not balanced stoichiometrically in order to facilitate the understanding and reading of the overall reaction mechanism. We may also note that we do not have any direct evidence at this point for the reversible formation of Co-doped ZnO (marked by asterisks in the above equations), not to mention the stoichiometry of such a reversibly formed phase. In fact, it may well be that zinc oxide and cobalt oxide are formed instead, as reported for spinel-structured ZnCo$_2$O$_4$.$^{[17b, 22]}$ Further complementary studies will have to be performed to clarify this aspect.

We may briefly summarize at this point the effect of introducing the cobalt dopant into the wurtzite zinc oxide structure. Most importantly, in particular regarding the application of such materials as alternative anode material for lithium-ion batteries, the presence of evenly distributed cobalt cations within the ZnO lattice$^{[10]}$ enhances the reversibility of the Li$_2$O formation and thus the reversible specific capacity. This beneficial effect presumably results from the presence of a percolating network of ultrafine metallic cobalt nanoparticles formed upon lithiation,$^{[8a, 23]}$ which ensures the required electron supply throughout the Li$_2$O matrix. Additionally, the Co-doping leads to an enhanced nanocrystallinity of the lithiated sample, thus constricting the formation of rather large LiZn and Zn$^0$ crystals. The latter aspect, in fact, appears to be of major importance for alloying materials in general, as previously reported for the commercial Sn-Co-C anode material composite,$^{[24]}$ employed in the ‘Nexelion’ battery (SONY), and also silicon-based lithium-ion anodes.$^{[25]}$

3.4 Galvanostatic Cycling and Rate Capability

The impact of the Co-doping of ZnO on the long-term galvanostatic cycling performance is presented in Figure 7. In the specific capacity vs. cycle number plot (Figure 7a) the positive effect of the doping in terms of achievable specific capacity and first cycle irreversible capacity loss, i.e., 42.6% for ZnO and 29.5% for Zn$_{0.9}$Co$_{0.1}$O, is immediately apparent. After some formation cycles, pure ZnO shows a stabilized reversible capacity of about 332 mAh g$^{-1}$ in the 30$^{th}$ cycle, which is close to the theoretical capacity of
ZnO considering only the reversible formation of the LiZn-alloy (≈ 329 mAh g⁻¹). The small fraction of extra capacity may be assigned to a partially reversible electrolyte decomposition as already reported for other transition metal oxides as well as the contribution of the conductive carbon. In fact, the potential profiles of selected cycles (Figure 7b) show a stepped shape related to the gradual de-/alloying process and no significant capacity in the high potential regime, in which the degradation of Li₂O occurs. Likewise, Co-doped ZnO shows a slight capacity fading during the initial cycles. However, after 40 cycles, Zn₀.₉Co₀.₁O reveals a stable performance providing a specific capacity of 762 mAh g⁻¹.

Figure 7. Constant current cycling of ZnO- (black) and Zn₀.₉Co₀.₁O-based (green) electrodes cycled at a specific current of 48 mA g⁻¹ (C/20); 1ˢᵗ cycle: 24 mA g⁻¹ (C/40). (a) Capacity vs. cycle number plot, (b) and (c) corresponding potential profiles of ZnO- and Zn₀.₉Co₀.₁O-based electrodes for selected cycles (2ⁿᵈ, 10ᵗʰ, 20ᵗʰ, 30ᵗʰ, 40ᵗʰ, 50ᵗʰ, 60ᵗʰ, and 70ᵗʰ).
The corresponding potential profiles, depicted in Figure 7c, exhibit a sloped profile as already stated above. Upon lithiation no particular features can be correlated with specific electrochemical reactions suggesting a catalytic effect of Co resulting in the promoted reduction of ZnO. However, in the low potential range of the charge profile similar features as the pure ZnO are observed. More importantly, for the delithiation process, at potentials above 1.5 V, a significant capacity is obtained, which, in accordance with the *in situ* XRD analysis presented herein, is ascribed to the degradation of Li₂O.

![Graph comparing rate capability of ZnO and Co-doped ZnO](image)

**Figure 8.** Comparison of the rate capability of electrodes based on ZnO (black, diamonds) and Co-doped ZnO (green, circles) nanoparticles.

To evaluate the rate capability of ZnO in comparison with Zn₀.₉Co₀.₁O, a multi-rate cycling test was conducted (Figure 8). The plot of the specific charge capacity vs. the applied current density demonstrates once more the superior specific capacity provided by the Co-doped ZnO, in particular compared to pure ZnO. Nevertheless, for very high current densities the delivered capacity decreases dramatically, indicating the need for enhanced electrode composite architectures as, for instance, the incorporation of secondary carbon nanostructures like graphene or carbonaceous coatings.²⁷
4. Conclusions

Pure and Co-doped ZnO were synthesized and structurally, morphologically, and electrochemically characterized. XRD, SEM, and TEM analyses revealed a reduction of the particle size, due to the introduction of the dopant, which is also evident from the smoother and broadened current peaks recorded by cyclic voltammetry. In order to elucidate the impact of the dopant on the lithium storage mechanism, electrochemical in situ XRD analysis of pure ZnO and Co-doped ZnO was performed. The results reveal a beneficial impact of the transition metal dopant on the electrochemical performance of ZnO by preventing the formation of large crystals and enhancing the reversibility of the Li$_2$O formation. Additionally, the reduction of the metal dopant presumably leads to an improved electronic conductivity within the lithiated particles. As a result, the reversible specific capacity initially approaches the theoretical value of 962 mAh g$^{-1}$. Long-term galvanostatic cycling further demonstrates the significant improvement of the achievable specific capacity. After 75 full dis-/charge cycles, electrodes based on Zn$_{0.9}$Co$_{0.1}$O show more than twice the capacity of pure ZnO, i.e., 789 mAh g$^{-1}$ vs. 326 mAh g$^{-1}$.

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References


Reversible conversion: The introduction of Co into the ZnO wurtzite structure results in a twice to thrice enhanced specific capacity by inhibiting zinc crystal growth upon (de-)lithiation, thereby, enabling the long-term reversible cycling of hybrid conversion/alloying-type lithium-ion anodes.