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

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Herein, an in-depth investigation of 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 (Zn₉₋ₓCoxO) were investigated comparatively. Characterization by using 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, which led to a decreased particle size for the doped compound. The in situ electrochemical XRD analysis of the first de-/lithiation of ZnO and Zn₉₋ₓCoxO revealed the highly beneficial impact of the transition-metal dopant on the reversible degradation of lithium oxide (Li₂O) and suppression of zinc crystallite growth upon lithiation; both effects are essential for greatly improved electrochemical performance. As a result, Co doping leads to a substantially increased specific capacity from 326 mAh g⁻¹ for pure ZnO to 789 mAh g⁻¹ for Zn₉₋ₓCoxO after 75 full charge–discharge cycles.

1. Introduction

Despite great technological interest in nanostructured zinc oxide (ZnO) for a large variety of applications, such as light-emitting diodes,[1] gas sensors,[2] or dye-sensitized solar cells,[3] their investigation as lithium-ion anode materials has been reported rather scarcely to date. In fact, although a theoretical specific capacity of about 988 mAh g⁻¹ (if the reaction ZnO + 3Li⁺ + 3e⁻ → LiZn + Li₂O is considered to be fully reversible) certainly arouses interest, apart from a few outstanding exceptions[4] most electrochemical studies revealed poor performance and rapid capacity fading.[5] To explain the origin of this inferior electrochemical performance of ZnO-based electrodes, Pelliccione and co-workers[6] very recently performed 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 the size of these particles exceeds a certain limit, the formation of ZnO accompanied by the degradation of Li₂O, that is, the conversion reaction, shows no further reversibility and only the alloying reaction of zinc with lithium takes place reversibly, which, in turn, is associated with the characteristic issues of alloying materials.[5]

In addition, the large volume changes upon alloying–dealloying lead to pulverization of the active material, ongoing electrolyte decomposition, and finally the loss of electrical contact within the composite electrode.[6] 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] which thus ensures 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.

Herein, we present an in-depth structural and electrochemical characterization of pure ZnO and Co-doped ZnO nanoparti-

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cles by using XRD, SEM, TEM, cyclic voltammetry (CV), and galvanostatic cycling techniques. Moreover, we performed a comparative in situ XRD analysis of Co-doped and pure ZnO nanoparticles. The obtained results, which are also discussed with respect to our previous findings for Fe-doped ZnO, 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.

**Experimental Section**

**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, with a total metal ion concentration of 0.2 M, was added dropwise under vigorous stirring to aqueous sucrose (1.2 M; ACROS ORGANICS). After continuous stirring for an additional 15 min at RT, the solution was heated to about 160 °C to remove the water. Concurrently, the sucrose started to become thermally decomposed. The remaining solid precursor was further dried at around 300 °C, then ground and calcined for 4 h under air at 400 °C (heating rate: 3 °C min⁻¹). Pure ZnO nanoparticles were prepared by following an analogous synthesis protocol in the absence of the Co precursor and using an annealing temperature of 450 °C.

**Morphological and Structural Characterization**

Powder X-ray diffraction (XRD) patterns were recorded by using a BRUKER D8 Advance with Cu Kα radiation (λ = 154 pm) and a step size of 0.0092°. Scanning electron microscopy (SEM) was carried out by 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) was performed by using a Philips CM 20 at 200 kV for Zn₀.₉Co₀.₁O nanoparticles samples deposited on a copper grid coated with a holey carbon film.

**Electrochemical Characterization**

Electrodes were prepared by dissolving sodium carboxymethyl cellulose (CMC, WALOCEL™ CRT 2000 PPA 12, Dow Wolff Cellulcosics) in deionized water (1.25 wt% of CMC in solution). Conductive carbon (Super C65™, IMERYS Graphite and Carbon) and ZnO or Zn₀.₉Co₀.₁O nanoparticles were added, which gave 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%), which served as a current collector, by using a laboratory doctor blade (wet film thickness: 120 μm). After an initial drying at RT overnight, disk electrodes (ø = 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-2008 eco glovebox (O₂ and H₂O content < 0.1 ppm), with lithium metal foil (Rockwood Lithium, battery grade) as the counter and reference electrodes. The electrodes were separated by a stack of polypropylene flosses (Freudenberg FS 2190), drenched with a 1 M solution of LiPF₆ in a mixture of ethylene carbonate/diethyl carbonate (UBE; 3:7 wt/wt). Because metallic lithium foil was used as the counter and reference electrodes, all potential values given herein refer to the Li/Li⁺ redox couple. Cyclic voltammetry and galvanostatic cycling were performed by using a VMP3 potentiostat (BioLogic) and a Maccor Battery Tester 4300, respectively. All electrochemical studies were conducted at (20 ± 2) °C in a potential range of 0.01–3.0 V.

**In situ XRD Analysis**

In situ XRD analysis of Co-doped and pure ZnO nanoparticles upon galvanostatic de-/lithiation was conducted by using a self-designed two-electrode in situ cell. Electrodes were prepared analogously to those used for the electrochemical characterization, with an overall composition of 65 wt% active material, 25 wt% conductive carbon, and 10 wt% CMC. The resulting mixture was dispersed by planetary ball-milling and cast onto a beryllium (Be) disk (thickness: 250 μm, Brush Wellman) that served concurrently as the current collector and “window” for the X-ray beam. The coated Be disk was dried for 30 min at 80 °C under ambient atmosphere and subsequently at 40 °C under vacuum overnight. Metallic lithium foil was used as the counter electrode. Two sheets of Whatman glass fiber drenched with a solution of LiPF₆ (1 M, 500 μL) in ethylene carbonate/diethyl carbonate (UBE; 3:7 wt/wt) were used as separator. The assembled cell was allowed to rest for 10 h prior to the in situ XRD measurements. Simultaneous galvanostatic cycling was performed by using a VSP potentiostat/galvanostat (BioLogic) and applying a specific current of ≈ 55 (Zn₀.₉Co₀.₁O) or 60 mA g⁻¹ (ZnO) and setting the cut-off potentials to 0.01 or 3.0 V. The XRD analysis was carried out in a 2θ range of 25–80° with a step size of 0.02758° and a time per step of 0.65 s. Consequently, every scan lasted exactly 30 min, which included an initial rest step of 419 s.

**2. Results and Discussion**

### 2.1. Structural and Morphological Characterization

The X-ray diffraction patterns of pure ZnO and Zn₀.₉Co₀.₁O presented in Figure 1, show the characteristic pattern of hexagonal-wurtzite-structured ZnO with the P₆₃mc space group (JCPDS file card no. 01-071-6424), which indicates the synthesis of phase-pure materials and the successful doping of ZnO with cobalt. The additional low-intensity reflections at about 2θ = 28.7, 31.1, and 32.7° (marked by *) originate from the diffraction of the CuKα radiation at the (100), (002), and (101) lattice planes, respectively. The Co-doped sample reveals slightly broader full width at half maximum values and lower reflection intensities compared with pure ZnO, which indicates a reduced crystallite size. These results are in excellent agreement with a recent in-depth crystallographic analysis, reported by Giulì et al.¹⁰

Figure 2 shows the SEM images of the pristine powderly samples. The SEM image of ZnO (Figure 2a) reveals a particle diameter of about 40 nm, whereas 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. The TEM micrographs of Co-doped ZnO shown in Figure 3 confirm this particle size and additionally reveal the 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, which further confirms the successful incorporation of the cobalt dopant into the wurtzite ZnO structure.

2.2. Cyclic Voltammetry

Figure 4 shows cyclic voltammograms of ZnO- and Zn\textsubscript{0.9}Co\textsubscript{0.1}O-based electrodes recorded between 0.01 and 3.0 V. In the first cathodic sweep, ZnO (Figure 4a) reveals three reduction peaks at potentials of 0.70, 0.38, and 0.13 V. 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. The peak at 0.70 V is commonly ascribed to the reduction of electrolyte components at the anode/electrolyte interface, which results in the formation of a solid-electrolyte interphase (SEI).\textsuperscript{[11]} The main peak at 0.38 V is mainly related to the reduction of ZnO to form metallic Zn and Li\textsubscript{2}O. At potentials below 0.2 V, the metallic Zn alloys with Li. However, the slope of the baseline is rather steep, which suggests that the lithiation processes might partially overlap. Upon delithiation, various peaks at 0.19, 0.29, 0.35, 0.54, and 0.68 V, one broad peak at 1.32 V, which probably consists of two overlapping peaks, and a low-intensity peak at 2.55 V were detected. The peaks in the low-potential region, that is, below 0.75 V, are related to the stepwise dealloying of LiZn as previously reported in literature.\textsuperscript{[5e, 12]} The underlying reaction corresponding to the broad, anodic peak at about 1.32 V remained unexplained for a long time.\textsuperscript{[5e]} Huang et al.\textsuperscript{[13]} recently ascribed this feature to the dealloying of LiZn. Moreover, they correlated the low-intensity peak at 2.55 V to the partially reversible degradation of Li\textsubscript{2}O accompanied by the formation of ZnO.\textsuperscript{[13]} Nevertheless, from studies on tin (oxide)-based anodes, it also appears possible to assign peak e) to the partially reversible formation of Li\textsubscript{2}O\textsuperscript{[7b]} and peak f) to a partial degradation of SEI components,\textsuperscript{[14]} particularly with respect to its absence in case of carbon-coated ZnO.\textsuperscript{[15]} However, we will discuss the assignment of peaks to specific electrochemical reactions in more detail with reference to the in situ XRD analysis presented hereafter. During subsequent sweeps, shown in Figure 4b, new cathodic peaks at 0.96 and 0.78 V arose, whereas the anodic peak at 2.55 V completely vanished; 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.\textsuperscript{[14]} In addition, peaks g), h), b), c), and e) show a shift towards slightly lower potentials and a considerable intensity decrease, and peak g) completely disappeared after a few cycles. Moreover, peak b) split into two peaks, which are assigned to the alloying reaction of Zn.

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, \textit{P}6\textsubscript{3}mc space group) is given below.

Figure 2. SEM micrographs of a) pure ZnO and b) Co-doped ZnO nanoparticles at a magnification of 100x.

Figure 3. (HR)TEM micrographs of Co-doped ZnO nanoparticles at different magnifications.
with Li; thus, the stepwise alloying becomes more apparent. In contrast, the peaks in region d) related to the dealloying processes remain relatively unchanged, although they reveal a slightly decreasing intensity. In fact, these results reveal the often-reported irreversibility of Li$_2$O degradation and the limited reversibility of the Li-alloying process of Zn.$^{[15a–e,6]}$

In Figure 4c, the first potentiodynamic cyclic sweep for Zn$_{0.8}$Co$_{0.2}$O is presented. Co-doped ZnO exhibits characteristics similar to undoped ZnO. However, the features are much less pronounced, which might be due to the smaller particle and crystallite size revealed by SEM (Figure 2) and XRD (Figure 1), and slightly shifted to higher potentials, which presumably results from enhanced electronic conductivity.$^{[16]}$ Analogous to ZnO, as described above, the SEI formation occurs at about 0.72 V, followed by reduction of ZnO at 0.46 V. Below 0.25 V, 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, that is, Co is reduced at higher potentials. However, no clear feature related to the reduction of Co was observed by performing CV, which is expected given the 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 with pure ZnO. During the anodic sweep, the dealloying of Zn occurs in the potential range between 0.16 and 0.74 V, followed by the degradation of Li$_2$O at 1.35 V, as mentioned previously. In subsequent cycles, peaks a) and b) vanish and new features appear at 0.93 and 0.81 V (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. However, compared with ZnO, Zn$_{0.8}$Co$_{0.2}$O shows a remarkably improved reversibility, particularly for peak e).

2.3. In Situ XRD

To further study the structural changes and phase transitions that occur 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 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 and D and E for the subsequent charge). To provide an overview of the evolution of the simultaneously recorded XRD patterns, a waterfall diagram that shows 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 processes that occur therein, 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), which indicates an incipient reduction in the long-range order within the wurtzite structure. This structural change is accompanied by some electrolyte decomposition, indicated by a slight change in the slope of the discharge curve, which is in good agreement with the CV results (Figure 4a). Although somehow expected, the initial reduction of the oxide is of particular interest because it is in contrast with our earlier finding for Fe-doped ZnO$^{[16]}$ 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 an insertion of lithium ions into the wurtzite structure may occur prior to the onset of the voltage plateau, favored by the presence of cationic vacancies in Zn$_{0.8}$Fe$_{0.2}$O as proposed by Giuliani et al.$^{[16]}$ A careful analysis of the different XRD patterns also reveals the appearance of a very broad and yet tiny reflection at about 43.0° (marked by a red arrow). Given the indicated reduction of ZnO accompanied by the formation of amorphous Li$_2$O,$^{[16a–i,7,18]}$ 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 that correspond to ZnO and Zn$_2$O, 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 last one is initially present as a shoulder of the Zn$_2$O-related reflection and subsequently continuously increasing in intensity, whereas the Zn$_2$O-related reflection itself vanished simultaneously. Their positions and relative intensity are in very good agreement with the JCPDS file no. 01-071-9525 reported for Li$_{1.5}$Zn$_{0.5}$O$_{2.25}$, which indicates that along the voltage plateau the previously formed metallic zinc also starts to alloy electrochemically with lithium and thus forms a Li$_2$Zn alloy phase with a rather low lithium content, that is, 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 almost simultaneously, that is, at the same voltage. At the end of the voltage plateau, in scan 19, the reflections that correspond to the wurtzite-structured oxide completely vanish and only the Li$_2$Zn-related reflections remain.

In region C, no significant changes are observed for scans 19–22, that is, along the initial rather steep voltage decrease. Subsequently, however, the intensity of the two reflections at about 37.0 and 42.7° that correspond to the Li$_2$Zn (x ≈ 1) phase decrease in intensity, whereas the one at around 41.0° continuously increases and initially shifts to slightly larger 2θ values and then back to slightly lower 2θ values. Indeed, when the extended 2θ range (up to 80.0°) was analyzed, it revealed that this shifting and increase in intensity is related to
the appearance of the fully lithiated LiZn alloy phase because from scan 2, new reflections also appear at around 48.5, 60.0, and 75.0°. This is in excellent agreement with the JCPDS card file no. 03-065-3016 reported for LiZn. In addition, further lithiation, that is, 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.\[^{56,12,19}\]

Finally, in scan 28, only reflections that correspond to the LiZn phase are present, which indicates that the lithiation reaction is complete 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, which indicates 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 the slope), the reflections that correspond to the Li\(_x\)Zn (\(x < 1\)) phase reappear and steadily increase in intensity, whereas the reflections related to the LiZn phase keep decreasing. In scan 35, at the end of region D, only the reflections that correspond to the Li\(_x\)Zn phase remain. However, these reflections abruptly vanish for the next scan (scan 36) as shown in Figure 5g (region E), in which scan 35 is also included for 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) because the alloying contribution for ZnO theoretically corresponds to 329 mAh g\(^{-1}\) 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 reoxidation of metallic zinc at potentials higher than 0.7 V.\[^{20}\] This is further supported by the appearance of a very broad reflection in the range of 31.0 to 35.0° and the limited decrease in intensity of the reflection at about 36.2° because it overlaps with the main reflection of the wurtzite-structured oxide. Nevertheless, this reoxidation process appears to be limited (see also Fig-
ure 4b) because very intense reflections that correspond to metallic zinc remain even at the end of the charge process at 3.0 V. Additionally, the specific capacity obtained over this voltage range is substantially lower than theoretically expected, given the fully reversible conversion of Li$_2$O ($\approx$ 416 mAh g$^{-1}$ rather than 658 mAh g$^{-1}$). Based on the above-described findings, we may qualitatively describe the multistep process as follows:

A) ZnO + Li$^+$ + e$^-$ $\rightarrow$ ZnO + Li$_2$O + Zn$^0$
B) ZnO + Zn$^2$ + Li$^+$ + e$^-$ $\rightarrow$ Li$_2$Zn + Li$_2$O
C) Li$_x$Zn + (1-x)Li$^+$ + (1-x)e$^-$ $\rightarrow$ LiZn
D) LiZn $\rightarrow$ Li$_x$Zn + (1-x)Li$^+$ + (1-x)e$^-$ $\rightarrow$ Zn$^0$ + Li$^+$ + e$^-$
E) Zn$^0$ + Li$_2$O $\rightarrow$ Zn$^0$ + ZnO + Li$^+$ + e$^-$

In summary,

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

Please note that the equations for the single regions are not balanced stoichiometrically because an adjustment with unknown general valencies would certainly only complicate the understanding and reading substantially without adding any beneficial further information. Additionally, the electrode chemistry presented for each step focuses only on the reactions that take place in the corresponding potential range. We may note at this point that our findings obtained by performing in situ XRD are in excellent agreement with the very recent in situ XAFS study by Pelliccione et al.,[6] who also observed a fully reversible LiZn formation in the first cycle, but observed incompleteness of the subsequent reoxidation of metallic zinc upon delithiation, which was presumably related to the formation of relatively large metallic zinc particles ($\approx$ 10–20 nm) and the corresponding extensive structural reorganization in the electrode, which was further supported by a very recent in situ TEM study.[21]

To investigate the effect of introducing the cobalt dopant into the wurtzite structure, we also carried out an in situ XRD analysis for Zn$_{0.9}$Co$_{0.1}$O-based electrodes (Figure 6). The corresponding potential profile is presented in Figure 6a whereas the overview of the evolution of the recorded XRD patterns is given in Figure 6b.

Again, the potential profile can be subdivided into five different regions (indicated by the highlighted scans), similar to the analysis of ZnO. Although the larger number of scans is a result of the slightly lower specific current applied (55 vs. 60 mA g$^{-1}$ for ZnO), two major differences are evident. The potential profile is generally smoother, that is, it shows less remarkable changes in slope, which may originate partially from the smaller initial crystallite size,[10a,b] and is in good agreement with the cyclic voltammetry results shown in Figure 4 and the slightly higher potential of the main voltage plateau upon discharge. The latter may be assigned to the higher reduction potential of cobalt compared with zinc.[20] However, 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, which indicates that for Co-doped ZnO the oxide is also 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.[15a] and reveals that, in contrast to iron, cobalt is purely divalent and, therefore, does not require the presence of, for example, cationic vacancies to balance trivalent cations in the oxide lattice. In addition, starting from scan 6, that is, at the onset of the subsequent voltage plateau the appearance of a very broad yet tiny reflection in the range of 41.0 to 45.0$^\circ$ is observed. Its intensity further increased during the following scans (Figure 6d, region B), whereas the oxide-related reflections continuously decrease until they completely vanish at the end of the voltage plateau (scan 22). Remarkably, however, in contrast to ZnO, no pronounced reflections are observed for the newly appearing reflection in the range of 41.0 to 45.0$^\circ$ and the intensity remains substantially lower in general. In fact, it appears that this rather broad new feature may be composed of two reflections, which presumably correspond to the concurrent formation of metallic Zn$^0$ and Li$_x$Zn (at $\approx$ 43.0 and 42.0$,^\circ$, respectively), which largely overlap. These findings provide two important pieces of information: First, the crystallinity of the formed phases is substantially lower than in ZnO (similarly to the findings for Fe-doped ZnO[20]), which indicates that, apart from the slightly smaller crystallite size of the pristine oxides (see Figure 2), the presence of cobalt as a dopant prevents the formation of large crystalline particles upon lithiation and thus favors the nanocrystallinity of the sample. Second, the introduction of the cobalt dopant appears to favor the formation of the Li$_2$Zn alloy kinetically. These two findings are, in fact, of particular interest because Su et al.[21] very recently reported that the growth of Zn particles and the alloying reaction are two competing processes that depend on the applied current density. We may thus assume that the formation of a continuous percolating network of metallic cobalt leads to enhanced electron transport and distribution within the initial nanoparticles, which favors the alloying reaction rather than zinc crystal growth.

Upon further lithiation (Figure 6e, region C), from scan 31 a new reflection appears at about 41.0$,^\circ$, which is in excellent agreement with the results obtained for ZnO and indicates the formation of the Li$_2$Zn 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), as seen for ZnO. Nevertheless, the dealloying reaction is apparently completed at relatively higher potentials ($\approx$ 1.2 V compared with $\approx$ 0.7 V for ZnO; see Figures 5a and 6a, respectively). Also, it appears that for Zn$_{0.9}$Co$_{0.1}$O in region E (Figure 6g) some Li$_x$Zn (x $\ll$ 1) phase remains, as indicated by the shoulder of the reflection at about 43.0$,^\circ$; the latter is 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 because no significant additional reflections were observed for this sample. In either case, this rather broad re-
flection 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 to 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, that is, 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 for both zinc and 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) \( \text{Zn}_0.9\text{Co}_{0.1}\text{O} + \text{Li}^+ + e^- \rightarrow \text{Zn}_0.9\text{Co}_{0.1}\text{O} + \text{Co}^{2+} + \text{Zn}^{2+} + \text{Li}_2\text{O} \)

B) \( \text{Zn}_0.9\text{Co}_{0.1}\text{O} + \text{Zn}^{2+} + \text{Li}^+ + e^- \rightarrow \text{Li}_x\text{Zn} + \text{Co}^{2+} + \text{Zn}^{2+} + \text{Li}_2\text{O} \ (x \ll 1) \)

C) \( \text{Li}_x\text{Zn} + \text{Zn}^{2+} + \text{Li}^+ + e^- \rightarrow \text{LiZn} \)

D) \( \text{LiZn} \rightarrow \text{Li}_x\text{Zn} + \text{Zn}^{2+} + \text{Li}^+ + e^- \)

E) \( \text{Li}_x\text{Zn} + \text{Zn}^{2+} + \text{Co}^{2+} + \text{Li}_2\text{O} \rightarrow \text{Zn}_{1-x}\text{Co}_x\text{O}^* + \text{Li}^+ + e^- \ (y \approx 0.1) \)

In summary,

\( \text{Zn}_0.9\text{Co}_{0.1}\text{O} + 2.9\text{Li}^+ + 2.9 \text{e}^- \rightarrow 0.9 \text{LiZn} + \text{Co}^{2+} + \text{Li}_2\text{O} \ (\approx 962 \text{ mAh g}^{-1}) \)

Please note that in this case the equations for the single regions are not balanced stoichiometrically to facilitate the understanding and reading of the overall reaction mechanism. We also note that we do not have any direct evidence at this point for the reversible formation of Co-doped ZnO (marked by * 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$_4$.[24,25] Further complementary studies will have to be performed to clarify this aspect.

At this point, we briefly summarize 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 materials 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,[9a,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, which constrains the formation of rather large LiZn and ZnO 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[25] employed in the “Nexelion” battery (SONY), and also silicon-based lithium-ion anodes.[26]

### 2.4. 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 versus cycle number plot (Figure 7a), the positive effect of the doping in terms of achievable specific capacity and first cycle irreversible capacity loss, that is, 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 30th cycle, which is close to the theoretical capacity of ZnO if only the reversible formation of the LiZn alloy ($\approx$ 329 mAh g$^{-1}$) is considered. The small fraction of extra capacity may be assigned to a partially reversible electrolyte decomposition, as already reported for other transition-metal oxides, and also the contribution from the conductive carbon.[26] 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, at which the degradation of Li$_2$O occurs. Likewise, Co-doped ZnO shows slight capacity fading during the initial cycles. However, after 40 cycles, Zn$_{0.9}$Co$_{0.1}$O reveals a stable performance that provides a specific capacity of 762 mAh g$^{-1}$.

The corresponding potential profiles, depicted in Figure 7c, exhibit a stepped profile as already stated above. Upon lithiation, no particular features can be correlated with specific electrochemical reactions, which suggests a catalytic effect of Co that results in the promoted reduction of ZnO. However, in the low-potential range of the charge profile, features similar to the pure ZnO are observed. More importantly, for the delithiation process a significant capacity is obtained at potentials above 1.5 V that is ascribed to the degradation of Li$_2$O, in accordance with the in situ XRD analysis presented herein.

To evaluate the rate capability of ZnO in comparison with Zn$_{0.9}$Co$_{0.1}$O, a multi-rate cycling test was conducted (Figure 8). The plot of the specific charge capacity versus the applied specific current demonstrates once more the superior capacity provided by the Co-doped ZnO, particularly compared with pure ZnO. Nevertheless, for very high specific currents the delivered capacity decreases dramatically, which indicates the need for enhanced electrode composite architectures, such as the incorporation of secondary carbon nanostructures like graphene or carbonaceous coatings.[27]

### 3. Conclusion

Pure and Co-doped ZnO were synthesized and characterized structurally, morphologically, and electrochemically. XRD, SEM, and TEM analyses revealed a reduction in 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. 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 Li2O formation. Additionally, reduction of the metal dopant presumably leads to enhanced 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 a significant improvement in the achievable specific capacity. After 75 full discharge/cycle charges, electrodes based on Zn0.9Co0.1O show more than twice the capacity of pure ZnO, that is, 789 mAh g⁻¹ versus 326 mAh g⁻¹.

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