Influence of cobalt concentration on CuO nanoplates morphology and its superior performance as Li-ion battery anode

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Abstract
Attracted by high theoretical capacity, CuO has emerged as a promising anode for Li-ion batteries. However, poor electronic conductivity, cycling instability and first cycle irreversibility is still a hindrance for end-application. To address these concerns in battery applications, for the first time, cobalt induced CuO nanobelt-like morphology is reported. Cobalt concentration dependent nanoplate morphology, reversibility and cycling stability have been investigated. Combined XPS and energy dispersive X-ray analysis indicates that the cobalt exist more in the bulk and very minimally on the surface. The 6 wt% Co in CuO nanobelt-like morphology showed excellent improvement in performance delivering 665 mAh g\(^{-1}\) at the end of 80 cycles at 1 C rate along with first cycle Coulombic efficiency of 66.1%. Impedance analysis confirms Co-CuO electrodes exhibited lower charge transfer resistance and better kinetics compared to bare-CuO. This electrode was paired with LiMn\(_2\)O\(_4\) cathode as full-cell Li-ion battery, which retained 385 mAh g\(^{-1}\) of capacity at the end of 100 cycles at 1 C rate.

1. Introduction
Over the past few decades, Li-ion batteries (LIBs) have become the most demanding power sources for applications like cellular phones, laptops, electric vehicles, hybrid EVs and all other battery back-up devices [1–4]. This is mainly because of their remarkable properties such as long cycle life, high energy density, low price, light weight and higher reversible capacity [5–8]. In the current scenario of LIBs, the most commonly used anode material is graphite that faces certain limitations owing to its low theoretical capacity (372 mAh g\(^{-1}\)) and poor Li-ion rate capability [9, 10]. Based on recent studies, transition metal oxides (TMOs) have become eminent anode materials for LIBs mainly due to their high theoretical capacities and rate capability based on conversion reaction with lithium ions [11–15]. Among all the TMOs, copper oxide (CuO) has become a potential candidate due to its attracting properties like high theoretical capacity (674 mAh g\(^{-1}\)), non-toxicity, easy to synthesize at low temperature, less energy consumption, low price and abundance in nature [16, 17]. Unfortunately, the main practical limitations of CuO are poor electronic conductivity, cycling instability, large first cycle irreversible capacity which leads to poor Coulombic efficiency and capacity fading occurred during the lithiation/delithiation [18–20]. To overcome these issues, several effective methods are adopted to fabricate nanostructured CuO as nanofibre [21], nanorods [22], nanoplate [23], nanoflake [24] and so on. Such nano-structuring will help in creating a better diffusion paths for Li\(^+\) due to high contact area between the electrode and electrolyte. However, doping in CuO is not explored extensively, Zn-doped CuO [25] and Mn-doped CuO [26] have been investigated for optical and magnetic applications and even Co-doped CuO have been reported for catalytic applications [27, 28]. There are limited reports available on the effect of doping CuO for Li-ion battery applications [29] specifically, cobalt introduced CuO nanostructures has not been reported so far.

The aim of the present work is to investigate the effect of cobalt in CuO, specifically for Li-ion storage. It is realized that the CuO nanoplate morphology synthesized by a facile hydrothermal technique transforms to a
nanobelt-like morphology upon introduction of cobalt into the lattice. The effect of such a morphology transformation on specific capacity and electrochemical stability is investigated. Though the morphology transformation was found to be nano-belt-like for all three samples with varying cobalt concentration, the electrochemical performance had a significant effect. Electrode with 6 wt% of cobalt outperformed the pristine and other cobalt concentrations investigated here. The best sample (6 wt% Co) was observed to have a retention of about 85% of its initial capacity at the end of 80 cycles tested at 1 C rate.

2. Materials and methods

Cupric chloride (CuCl₂ · 2H₂O), sodium hydroxide pearl (NaOH, Nice Chemicals Ltd, India), Graphene nanoplatelet (Reinstein NanoVentures, India) and cobalt (II) acetate tetrahydrate ((CH₃COO)₂Co · 4H₂O Sigma Aldrich) were utilized as received for the present work. In a typical process, 1 g of NaOH in 25 ml of deionized (DI) water is drop wise added to 25 ml of 4.262 g of CuCl₂ solution. As obtained copper hydroxide (Cu(OH)₂) black precipitates were centrifuged and dispersed in concentrated NaOH (15 M). The solution was kept for overnight stirring until complete dissolution. The uniform solution was autoclaved at 80 °C for 12 h. After hydrothermal, the final precipitates were centrifuged and washed with DI water until neutral pH. The product was kept at 70 °C until dried. To investigate the influence of cobalt in CuO nanoplates, we prepared by following the same synthesis except the addition of cobalt precursor (cobalt acetate tetrahydrate) in different weight ratios 0 wt% (bare CuO), 3 wt%, 6 wt%, and 9 wt% with constant vigorous stirring prior to hydrothermal process. Samples were abbreviated as CuO_Co-0%, CuO_Co-3%, CuO_Co-6% and CuO_Co-9% respectively. Structural analysis were studied using X-ray diffraction (Rigaku-Japan), while surface chemical analysis was investigated using X-ray photoelectron spectroscopy (XPS-Axis Ultra, UK, Al Kα). High Resolution Transmission Electron Microscopy (HRTEM, FEI TECNAI G²-30, operating voltage 200 kV) was carried out in order to determine the size and morphology of CuO nanoplates and energy dispersive X-ray analysis (EDAX) for composition analysis. The electrodes for electrochemical evaluation were fabricated using the slurry casting technique. Slurry was prepared by mixing the active material with polyacrylic acid (PAA) as binder and graphene nanoplatelets as conductive carbon additive in the weight ratio 70:10:20 respectively with ethanol as the solvent. Doctor-blading was done onto a copper foil and the electrode was then pressed prior to cell fabrication. Glass microfiber was used as separator and lithium foil was employed as the counter electrode. 1 M lithium hexafluorophosphate (LiPF₆) dissolved in ethylene carbonate and dimethyl carbonate (ratio 1:1 vol.%) is utilized as electrolyte (PuriEL, Canada). The half-inch diameter Swagelok cell or 2032 coin cells were assembled inside an argon-filled glove box. Galvanostatic charge/discharge was done using Biologic (USA) or Arbin Instruments (USA) at different C-rates over the range 0.05—3 V at room temperature. The impedance measurements were carried out using the Biologic in the frequency range of 10 mHz to 10 kHz with 10 mV ac amplitude. The full-cell was demonstrated with LiMn₂O₄ cathode with 80:10:10 ratio (active materials: carbon black: pvdf) and slurry casted on aluminum foil. The full-cell assembled was based on the capacity ratio of cathode to anode CₓCathode/CAnode = 1.2 and it was cycled at 1 C rate based on the anodes active weight.

3. Results and discussion

3.1. Structure and morphological

The XRD diffraction patterns of CuO_Co-X% (here X = 0, 3, 6, 9 wt% of cobalt) samples are shown in figure 1. The XRD pattern shows that all the four samples are highly crystalline with intense peaks at (−111) and (111) [21]. Diffraction peaks corresponds to monoclinic structure of CuO. This confirms that even after cobalt precursor addition there is no change in crystal structure. Minor peak at 46.1° is possibly not due to the introduction of cobalt as they are present even in CuO sample. The major peaks of the sample are predominantly CuO and no other copper oxide phases (such as Cu₂O or Cu₄O₃) are present as shows in figure S1 is available online at stacks.iop.org/MRX/6/125543/mmedia by comparing the peaks with the standard data sets. A weak peak at 20° could be assigned to CoO which corresponds to negligible quantity and hence we believe that majority of cobalt is in the bulk of CuO as confirmed by energy dispersive X-ray analysis (discussed later). The detailed surface morphological studies of the CuO_Co-X% samples were studied using TEM. Figures 2(a) & (b) represents the TEM and HRTEM images of the CuO while (c) & (d) represents the same for CuO_Co-6% samples. TEM/HRTEM images of the CuO_Co-3% and CuO_Co-9% samples are presented in figure S2 which also shows similar morphology of the CuO_Co-6% sample but with higher degree of agglomeration. From several LM-TEM images the width and length of the CuO_Co-0% and CuO_Co-6% nanoplates were measured and the distribution is displayed in the figure S3. The width and length of CuO is about 65 nm and 140 nm respectively while for the CuO_Co-0% width was about 40 nm and the length showed a bi-modal distribution of about 230 nm and 350 nm. Effectively, the width decreased a bit and the length increased almost twice that of the
bare nanoplates confirming the morphology becoming a nanobelt-like structure. The CuO_Co-0% width and length is however, similar to the nanoplate morphology that we have reported previously [23], as the same process is adopted for CuO_Co-0% nanoplate synthesis. HR-TEM on all the four samples confirms that the
nanoplates lattice fringes with d-spacing of 0.27 nm is comparable to standard values of (-111) planes of the monoclinic CuO phase.

3.2. Chemical analysis

XPS measurements were done to study the chemical composition and surface chemistry of CuO_Co-X% samples. The survey spectra are presented in figure S4(a) and the 284.6 eV peak for C 1 s is utilized for calibration. High resolution spectra of Cu 2p (figure 3(a)) indicates two main peaks at 933.7 eV and 953.8 eV corresponding to binding energies Cu 2p3/2 and Cu 2p1/2 respectively and peaks at 942.7 and 963.4 eV are attributed to Cu2+ satellite peaks. The major O 1 s peak at 529.5 eV are associated to O2- (figure 3(b)) and Co 2p3/2 peaks is not observed in all the samples possibly due to low concentration on the surface. However, CuO_Co-9% sample shows CoO-like (Co2+) features based on Co 2p3/2, 2p1/2 and satellite peaks at 780.2, 792 and 785.5 eV respectively (figure S4(b)). Even though, XPS spectra indicate a weak presence of cobalt on the surface, higher concentration is present in the bulk as observed by EDAX analysis. Figure S5(a) shows the TEM/EDAX spectra of CuO_Co-0% sample presence of elements like carbon, oxygen and copper are confirmed. Figure S5(b) shows the EDAX spectra of CuO_Co-6% sample and elements present are carbon, oxygen, cobalt and copper. Table S1 & S2 shows corresponding at.% of the elements present in both the samples. From the analysis it is clear that about 6.42 wt% of cobalt is present in the CuO_Co-6% sample. Here, the presence of carbon and higher copper content in the CuO_Co-6% sample could be due to the contribution from the TEM grid. This indicates the non-uniform distribution of cobalt in the CuO lattice. Yet, XPS & EDAX combined results confirm that cobalt is present in the bulk and not on the surface.

3.3. Half-cell Li-ion battery of CuO anodes

The electrochemical performance of CuO_Co-X% nanoplates were investigated based on galvanostatic charge-discharge cycles. The first cycle discharge-charge profiles of CuO_Co-X%, half-cells at 1 C rate is shown in figure 5(a). Samples show typical cycling performance of CuO, with phase transformation from CuO → Cu4O3 → Cu2O → Cu during discharge [23]. CuO_Co-0% sample delivered 1st cycle discharge/charge capacities of 1540/930 mAh g⁻¹ while the CuO_Co-3% sample delivered of 1689/1056 mAh g⁻¹. First cycle discharge/charge capacities of CuO_Co-6% and CuO_Co-9% are respectively 1359/898 mAh g⁻¹ and 907/587 mAh g⁻¹ respectively. Among the four, CuO_Co-6% shows highest Coulombic efficiency of 66.1% compared with other samples. Figure 5(b) shows the cycling performance for 80 cycles at 1 C rate for all the electrodes. Among all, CuO_Co-9% exhibits lowest capacity of 135 mAh g⁻¹ at the end of 80 cycles compared with the other three samples. CuO_Co-0%, CuO_Co-3% and CuO_Co-6% shows charge capacities of 248 mAh g⁻¹, 352 mAh g⁻¹ and 667 mAh g⁻¹ respectively at the end of 80 cycles. From the cycling performance it can be observed that CuO_Co-6% shows higher capacity and cycling stability at the end of 80 cycles. Table 1 represents a detailed comparison to evaluate the electrochemical performance of present set of samples and different nanostructures of previously reported CuO electrodes by various synthesis methods. It is clear that the present CuO_Co-6%
displays good cycling stability and capacity. Further from the Coulombic efficiency plot (figure 5(b)) it can be inferred that CuO$_2$-Co-6\% exhibits the maximum Coulombic efficiency (99\%) compared with the other CuO$_2$-Co-X\% nanoplates. Also CuO$_2$-Co-9\% shows least Coulombic efficiency close to 64.77\%. Figure S6a
shows the cycling data for CuO\textsubscript{Co-6\%} electrode at 5 C rate the result demonstrates 350 mAh g\textsuperscript{-1} capacity could be reversibly delivered at a high rate and a good retention of over 75% at the end of 100 cycles.

Rate performances of the four samples at different C-rates ranging from 1 C to 25 C, 5 cycles each is displayed in figure S6b. Rate test were done by limiting the discharge to 1 C while maintaining the charge at respective rates as indicated in the figure legends. As noted from the figure, CuO\textsubscript{Co-6\%} retains higher capacity than other electrodes even at 25 C rate (~ 200 mAh g\textsuperscript{-1}). Also after reverting the C-rate from 25 C back to 1 C, the electrode retained almost 85% of its initial capacity, denoting the better rate capability of the electrode. The other three electrodes show poor capacity retention at 25 C and recovery. This clearly indicates introducing cobalt into the CuO lattice is a potential approach to control the morphology and hence the electrochemical stability for Li-ion battery applications. To examine the electrochemical impedance of the four samples, the EIS measurements were done and the corresponding data are shown in figure S7. The EIS result illustrates a typical Nyquist profile for all the samples with a semicircle in the high-mid frequency region and a straight line at the low frequency region. It is obvious from the diameter of the semi-circle that the charge transfer resistance is lower as for the CuO\textsubscript{Co-6\%} electrode compared to that of the other three samples. The straight line in the low frequency region also has higher slope than other three samples indicating better Li-ion diffusion in the lattice. This improved Li-ion diffusion and fast charge transfer for CuO\textsubscript{Co-6\%} sample enables high performance. Based on the electrochemical results the performance of the CuO\textsubscript{Co-6\%} sample could be correlated very well with the morphology, agglomeration of the nanobelts and lower charge transfer resistance. As discussed above in the morphological analysis part using TEM, the introduction of cobalt into the lattice of CuO, the nano-plate morphology transforms to nano-belt-like. This leads to significant improvement in the electrochemical stability. However, there is an effect on the concentration of cobalt: for example CuO\textsubscript{Co-3\%} and CuO\textsubscript{Co-9\%} samples did not perform comparable to CuO\textsubscript{Co-6\%} sample though their morphology was also nano-belt-like. This could be explained based on the high-degree of agglomeration of the nano-belt-like structures probably leads to lacks electrical contact upon volume changes during cycling. It may be noted that apart from the high degree of agglomeration for CuO\textsubscript{Co-9\%} the belt-like morphology also seem to be dissociating (figure S2c). This leads to depressed structural phase transformation and poor capacity during lithiation/delithiation cycles which is also evidenced from the short voltage plateaus compared to other samples (figure 4) [23].

3.4. Full-cell Li-ion battery with CuO anodes

Though CuO anode have been investigated and reported by several research groups only few reports are available with CuO as anode in full-cell Li-ion batteries [37, 38]. This makes it important to demonstrate full-cell Li-ion batteries based on CuO as a anode material. To establish the use of high capacity CuO\textsubscript{Co-6\%} anode, we fabricated a full-cell Li-ion battery against a LiMn\textsubscript{2}O\textsubscript{4} cathode (results reported previously [39]). It may be noted that LiMn\textsubscript{2}O\textsubscript{4}-CuO full-cell Li-ion batteries have never been reported to the best of our knowledge and is a highlight of the present work. Figure 6(a) shows 1 C charge/discharge profiles and figure 6(b) shows its cycling stability for 100 cycles. The full-cell delivers an average voltage of 2.0 V and first discharge capacity of 650 mAh g\textsuperscript{-1} equivalent energy density of 1300 Wh kg\textsuperscript{-1} (based on anodes active weight). The 1\textsuperscript{st} cycle Coulombic efficiency (CE) was 62% while it can be improved further, it may be noted that in the subsequent cycles, CE climbed to almost 99.5% and maintained the same for 100 cycles. The slow decay in capacity is attributed to CuO anode and requirement of proper capacity matching. Yet, the cell retained a reasonable specific capacity of 385 mAh g\textsuperscript{-1} at the end of 100 cycles. Here, the potential of CuO anode in full-cell application is established as a proof of concept.

4. Conclusions

We report a facile and cost-effective hydrothermal technique for the synthesis of CuO\textsubscript{Co-X\%} nanoplates for the first time. XRD spectra confirms that even after cobalt precursor addition there is no change in crystal structure. From the morphological characterizations it is observed that the CuO nanoplates aspect ratio increased significantly upon cobalt addition and transforming the morphology to nanobelt-like structure. Electrochemical cycling and rate capability, revealed that an optimum cobalt concentration in CuO nanoplate is 6 wt% that delivered a specific capacity of 665 mAh g\textsuperscript{-1} and a Coulombic efficiency of 99.9% at the end of 80 cycles at 1 C rate. The poor stability of the other electrodes could be due to agglomeration and dissociation from belt-like morphology which leads to poor structural phase transformation during lithiation/delithiation cycles. As an end application, a full-cell Li-ion battery with CuO\textsubscript{Co-6\%} electrode as anode and spinel LiMn\textsubscript{2}O\textsubscript{4} as cathode was fabricated and tested. The full-cell displayed specific capacity of 650 mAh g\textsuperscript{-1} in the first discharge while maintaining almost 99.5% coulombic efficiency at the end of 100 cycles.
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Conflicts of interest

The authors declare no conflicts of interest.

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