

Experimental investigations of cyclic characteristics of binder-free nanostructured copper oxides as negative electrodes of lithium-ion batteries

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Received 3 May 2025 ♦ Accepted 20 June 2025 ♦ Published 30 December 2025

Citation: Ikram SMD, Rahman MdA, Billah MdM, Jui JA (2025) Experimental investigations of cyclic characteristics of binder-free nanostructured copper oxides as negative electrodes of lithium-ion batteries. *Modern Electronic Materials* 11(4): 259–266. <https://doi.org/10.3897/j.moem.11.4.157750>

Abstract

Nanostructured copper oxides (CuO, Cu₂O) are regarded as promising anode materials for lithium-ion batteries (LIBs) due to owing high theoretical specific capacity and efficient conversion reaction mechanism with lithium under moderate conditions. On investigating the cyclic characteristics of binder-free CuO/Cu₂O anodes at 1C current rate, first charge and discharge capacities were observed to be 455.4 and 431.9 mAh/g, respectively, with a Coulombic efficiency of 94.8 %. However, a gradual mitigated capacity was evident as the discharge capacity was decreased to 352.2 mAh/g by the 20th cycle, which can be attributed to solid electrolyte interphase (SEI) layer formation, electrode degradation, or loss of lithium. Beyond 20th cycles, the battery exhibited a more stable cycling regime, with Coulombic efficiency stabilizing ranging around 82–85 %. By the 40th cycle, discharge capacity was further declined to 339 mAh/g, indicating the ongoing degradation mechanisms, however at a much lower rate, such as SEI layer thickening and electrode pulverization. However, despite the initial instability, the system demonstrated enhanced consistency in later cycles, emphasizing the potential of nanostructured copper oxides as efficient LIB anodes. Future efforts should focus on mitigating long-term capacity fading to enhance performance and cycle life.

Keywords

copper oxides, Binder Free, nanostructured, anode, lithium-ion batteries (LIBs)

1. Introduction

Because of their exceptional energy density, extended cycle life, and lightweight design, lithium-ion batteries (LIBs) have emerged as the leading technology in portable devices, electric vehicles (EVs), and grid storage systems. Improving LIBs' electrochemical performance has become crucial due to the increasing need for high-performance energy storage systems brought on by developments in electric mobility and renewable energy inte-

gration [1]. To fulfill the ever-increasing energy demand and environmental goals, this has prompted a great deal of research into upgrading the materials used for both anodes and cathodes. Although graphite has been the most common material as negative electrode material, the hunt for alternative materials with greater capacity and better cyclic stability has been spurred by graphite's relatively low specific capacity and poor performance at higher charging rates [2].

In this context, copper oxides (CuO and Cu_2O) have emerged as promising candidates as anode material in LIBs due to their high theoretical specific capacity, vast abundance, and eco-friendliness. Copper (II) oxide (CuO) and copper (I) oxide (Cu_2O) exhibit distinct electrochemical characteristics that have been widely explored in battery applications [3]. CuO with a theoretical capacity of 674 mAh/g and Cu_2O with a theoretical capacity of 703 mAh/g, surpass graphite's theoretical capacity of 372 mAh/g offer attractive candidacy to be used in various high-energy-density applications [4]. Furthermore, copper oxides are abundant and fairly inexpensive, offering a sustainable alternative to rather expensive and less abundant materials such as silicon and tin [5]. Notwithstanding these benefits, copper oxides have several inherent constraints that often limit their efficient application in LIBs. The significant volume shift that occurs during the lithiation and delithiation processes is one of the main concerns, as it leads to structural deterioration and declined capacity over the extended number of cycles [6]. Furthermore, copper oxides' low electronic conductivity restricts their effectiveness at high current densities, making the employment of conductive additives or nanostructuring techniques necessary to enhance performance [7]. Again, the electrochemical cycling behavior may become even more complex due to the development of irreversible phases and side reactions, such as the conversion reaction between copper oxide and lithium [8]. All these elements act against copper oxides' long-term stability and usefulness in LIBs.

Considering these difficulties, a thorough examination of the cyclic properties of copper oxides such as their electrochemical impedance, rate capability, and capacity retention which are essential to create plans for improving their functionality. The electrochemical mechanisms of copper oxides have been the subject of several investigations, which have provided information on the intercalation and conversion procedures that take place during lithiation [9]. However, there is still a lack of thorough knowledge of their cyclic behavior, especially in practical working environments. By offering a methodical experimental examination of the cyclic performance of copper oxides as negative electrodes in lithium-ion batteries, this research seeks to close this gap.

This work investigates the variables influencing the cyclic performance and stability of copper oxide-based anodes using a variety of electrochemical experiments, such as charge-discharge cycling, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The main objective is to evaluate the influence of structural changes during cycling, rate capability and capacity retention, all of which are essential for comprehending the materials' long-term performance. The findings of this study will lead to developing methods for improving the electrochemical stability of copper oxides, including material modification, nanostructuring, and composite production, and will offer essential insights into the potential of these materials for real-world LIBs applications.

2. Experimental

2.1. Fabrication of nanoporous Cu-oxides

To ensure low electrical resistance and high conductivity, minimizing energy loss, copper (Cu) foil of 99.9 % purity was used for this study. After cleaning with acetone and drying in an air drier, two pieces of foils placed in quartz crucibles were heated from room temperature up to 250 °C and 350 °C in a furnace and both samples were subjected to thermal oxidation in air for 2 h. The temperature was maintained at the set value during oxidation precisely and then the furnace was turned off allowing the samples to get cooled down to room temperature slowly. Later, the shape, pore size and distribution of the resultant nanostructured Cu-oxides (NCu_xO_y) layers were evaluated following removal of the copper substrate cautiously. For the readers' convenience, Cu foils oxidized at 250 °C and 350 °C are referred to as N250- Cu_xO_y and N350- Cu_xO_y , respectively hereafter.

2.2. Characterization

The N250- Cu_xO_y and N350- Cu_xO_y samples were characterized using x-ray powder diffraction (XRD) to investigate the crystallographic data and especially identify the phases present. To account for various scattered and random orientations, scans were performed at different 2 θ angles, ranging from 10° to 90° with a step size of 0.05° using CuK_α radiation ($\lambda = 0.15406$ nm) from an Empyrean XRD system (Panalytical, Netherlands). Morphological and compositional analysis of the NCu_xO_y were conducted using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) attached to the SEM. All the images were recorded using a high-quality JSM 7600F instrument (JEOL, Japan) at 5.0 kV at various magnifications.

2.3. Electrochemical study

Coin cell battery cases (CR2032, supplied by Lith Co., China) were used for assembly for the current study. The anode samples consisted of 18 mm diameter and 0.1 mm thick (~ 2 cm²) NCu_xO_y , while the cathodes were LiCoO_2 -coated aluminum sheets. A 20 mm diameter battery-grade polyvinyl chloride (PVC) separator was placed between the electrodes. The PVC separator was used due to its excellent electrical insulating properties along with the chemical stability to prevent short circuits between electrodes as ions are conducted during the operational time of the LIBs. Both sides of the separator were soaked with a few drops of 1M LiPF_6 electrolyte (supplied by Ximen Tmax Battery Equipment Ltd., China), dissolved in a 3:7 volume ratio of ethylene carbonate (EC) and diethylene carbonate (DEC). The battery was then sealed air-tight by crimping at approximate-

ly 100 psi using a battery crimping machine (Metrology Lab, CUET).

3. Results and discussion

3.1. XRD analysis

XRD patterns of both the samples fabricated at different oxidation temperatures are presented in Fig. 1. Two distinct oxide phases, cubic Cu_2O (space group $Pn-3m$, JCPDS #05-0667) and monoclinic CuO (space group $C2/c$, JCPDS #45-0937), were identified for both samples. Cu_2O seems to be the dominant phase at a lower oxidation temperature of 250°C , with characteristics peaks positioned at $2\theta = 36.90^\circ, 43.40^\circ, 50.50^\circ, 74.50^\circ$, and 90.00° . As the oxidation temperature increased to 350°C , the CuO phase seems to be the dominant phase as evidenced from the increasing intensity of the CuO diffraction peaks, particularly the prominent peaks located at $2\theta = 35.70^\circ, 38.70^\circ$, and 66.60° . In addition, the presence of the low-intensity peaks can be attributed to the face-centered cubic Cu (space group $Fm-3m$, JCPDS #04-0836) due to partial exposure of the Cu substrate from non-uniform oxidation. The diffraction data were analyzed using Scherrer's formula,

$$D = 0.9\lambda / B \cos(\theta),$$

where λ is the X-ray wavelength, B is the full width at half maximum (FWHM) of the peaks and 2θ is the angle between the incident and diffracted beams.

The average crystal size of Cu_2O and CuO of N250- Cu_xO_y is found to be 100 nm and 160 nm, respectively. In contrast, the average crystal size of Cu_2O and CuO of N350- Cu_xO_y is found to be 150 nm and 180 nm,

respectively. It is noted that the average crystallite sizes of both Cu_2O and CuO increased with the increased oxidation temperature reflecting the improvement in crystalline quality and decreased micro-strain with reduced crystal imperfection due to higher solid-state diffusion [10–12]. Thus, a higher oxidation temperature leads to the formation of a larger amount of CuO as the dominant phase because of a higher degree of oxidation whereas a larger crystallite size results from the higher thermal energy for diffusion. The larger crystallite size of the CuO phase at both oxidation temperatures results because CuO is formed with a higher oxidation state of +2 compared to the lower oxidation state of Cu_2O with an oxidation state of +1. A higher oxidation state favors higher crystal size because of several factors including the increased phase stability and stronger interaction of copper ions with oxygen ions in the lattice promoting the growth of the larger crystallite size.

3.2. SEM & EDX analysis

Figure 2 shows the SEM and EDX spectra of N250- Cu_xO_y and N350- Cu_xO_y . It is noted that N250- Cu_xO_y exhibits a surface resembling an ocean mesh, akin to a circular ripple, with forming wave crests and radial streaks, accompanied by a light sea spray mist above the surface as shown in Fig. 2a. In addition, the surface morphology of N350- Cu_xO_y entirely changed to a porous structure with catkin as shown in Fig. 2b. Usually, it is expected that higher oxidation temperatures should result in a denser structure. However, here a more porous surface morphology at a higher oxidation temperature can result from several factors like thermal stress and a faster oxidation rate. At higher oxidation temperatures the differential thermal expansion between the copper foil and the oxide layer can induce thermal stress leading to increased porous structure. The faster oxidation rate also can contribute to

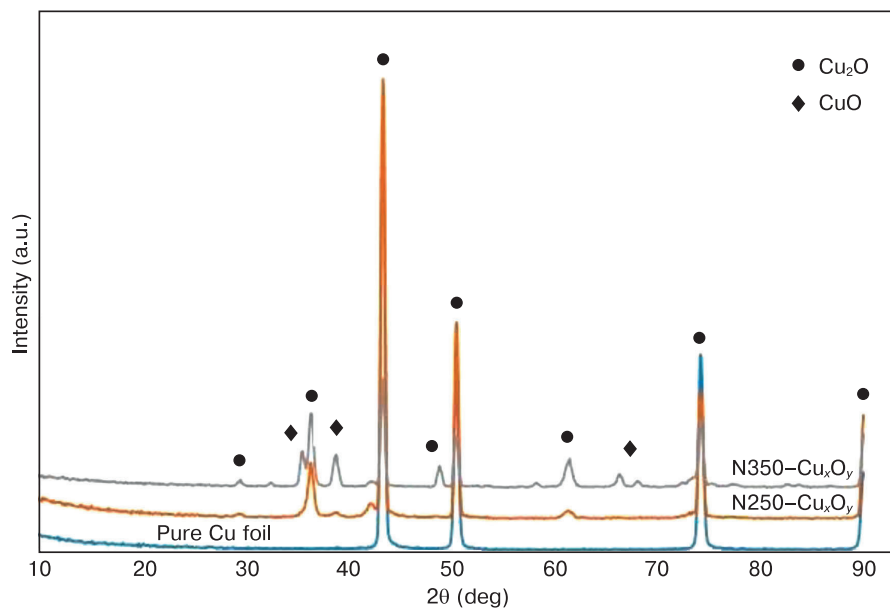


Figure 1. XRD patterns of Cu foils oxidized at 250°C and 350°C for 2 h

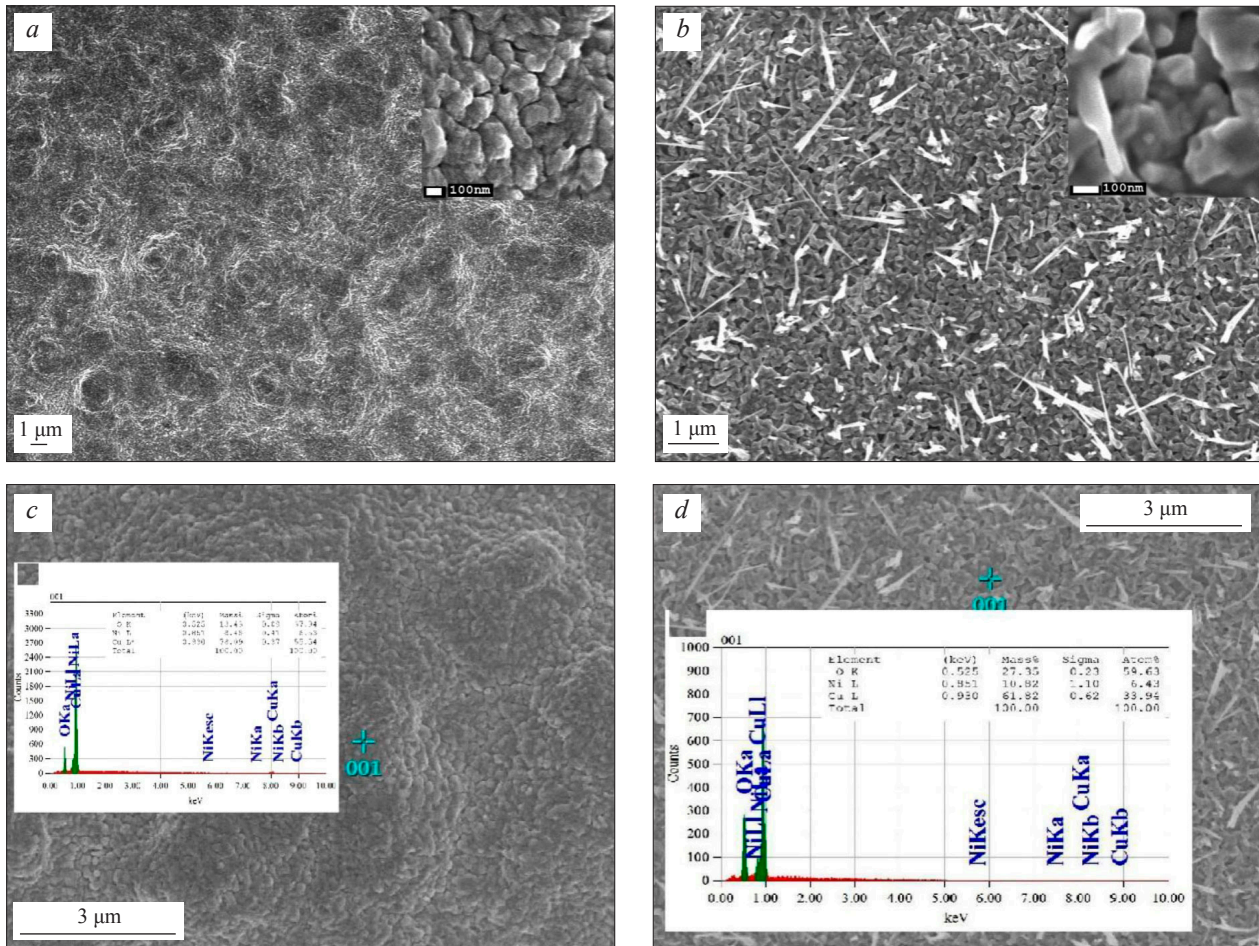


Figure 2. SEM and EDX images of (a, c) N250-Cu_xO_y and (b, d) N350-Cu_xO_y (insets show the high magnification images)

the more porous morphology differential oxidation rate across the thickness of the oxide layer.

However, the higher magnification image of N350-Cu_xO_y exhibits a more polished surface compared to N250-Cu_xO_y due to the more efficient oxidation process, improved atomic diffusion, and the formation of a more uniform and continuous oxide layer [13–15]. More smoother surface morphology even with higher porosity evident in the presence of small size evenly distributed porosity for the oxide layer oxidized at higher oxidation temperature.

3.3. Electrochemical performance

Figure 3 shows the change of cell current and voltage with respect to the time when N350-Cu_xO_y was used as the anode of the LIB. It shows the change of current and voltage with respect to time in Fig. 3a for 1–20 and in Fig. 3b for 21–40 charge-discharge cycles.

It is to be noted that the assembled coin cell with N250-Cu_xO_y as an anode of LIB was not electrochemically cycled due to a very small amount of oxide formation and loose connections of oxides with Cu foil. The above-discussed characterization also showed that the oxide formed at an oxidation temperature of 350 °C was of better quality with a higher degree of crystallinity.

Hence, we discarded the lower-temperature oxidation sample for further analysis. During the charge-discharge cycles, copper oxides undergo electrochemical reactions where lithium ions intercalate the anode during charging and leave the anode during discharging. During the discharging cycle, lithium ion is oxidized at the anode and forms metallic Cu at anode and Li₂O at cathode. The plotted data represents galvanostatic charge-discharge cycles, where voltage pulses were applied, and the current response was measured. The sharp peaks in the current correspond to the rapid lithium-ion insertion/extraction, while the gradual decay indicates diffusion limitations and internal resistance effects. Some points are higher because of variations in the electrochemical kinetics, including differences in Li-ion diffusion, surface reactions, and resistance changes as the electrode material undergoes structural transformations. The progressive decrease in peak height suggests capacity is fading, which can result from material pulverization, loss of electrical contact, or side reactions.

Figure 4 shows the differential capacity (dQ/dV) vs. voltage for a LIB with copper oxides (N350-Cu_xO_y) as the anode and LiCoO₂ as the cathode. The two graphs correspond to electrochemical impedance spectroscopy (EIS) data, taken at two different states of the battery: Fig. 4a is for the fresh cell before cycling, showing the

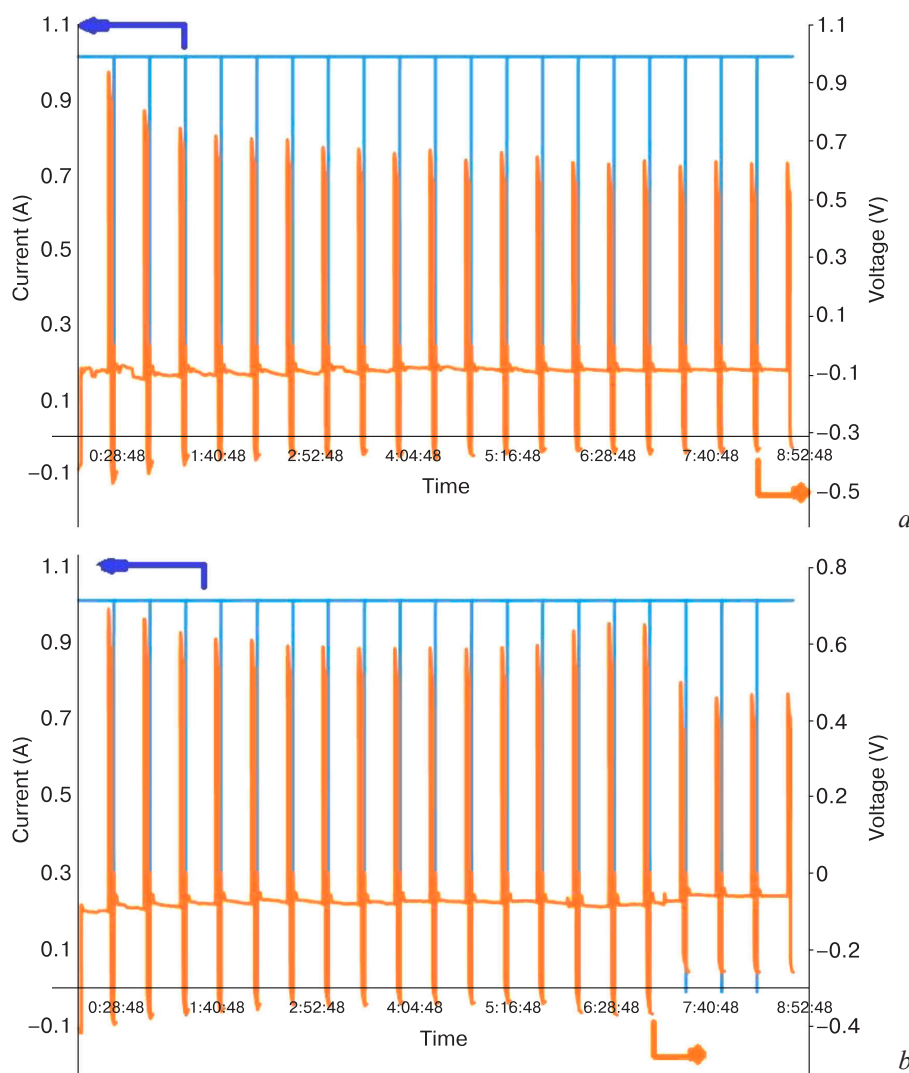


Figure 3. Change of current and voltage with respect to time: (a) 1–20 and (b) 21–40 charge-discharge cycles

initial electrochemical behavior, and Fig. 4b is obtained after 40 charge-discharge cycles displaying changes due to cycling. It is to be noted that the wider, symmetric triangular shape indicates that the battery initially has a well-defined electrochemical response in Fig. 4a. It indicates a highly reversible electrochemical reaction means charge and discharge behavior is quite consistent. In addition, the multiple peaks suggest distinct redox reactions, likely corresponding to the lithiation and delithiation of CuO or Cu₂O and LiCoO₂. Also, the steep nature of the curves may indicate low internal resistance and high lithium-ion mobility in the fresh cell [16]. In contrast, after 40 charge-discharge cycles, the curves become more asymmetric and narrower, indicating increased resistance and capacity fading over cycling, as shown in Fig. 4b. A noticeable shift in the peaks suggests a change in reaction kinetics, likely due to SEI layer formation, electrode degradation, or lithium plating. In addition, the increased broadness in dQ/dV peaks indicates possible irreversible side reactions or electrode structural changes affecting charge storage [17]. However, the higher resistance (steeper

voltage shifts) at low voltages suggests the development of passivation layers, electrode pulverization, or loss of active material [18, 19].

Figure 5 shows the change of specific capacity and coulombic efficiency during (a) 1–20 and (b) 21–40 charge-discharge cycles at 1C current rating. Figure 5a represents the specific capacity (mAh/g) vs cycle number for the first 20 charge-discharge cycles. The blue and orange lines likely correspond to the charge and discharge capacities, respectively, while the gray curve represents the Coulombic efficiency (%). The 1st cycle charge and discharge capacity are observed to be 455.4 and 431.9 mAh/g, respectively, with a Coulombic efficiency of 94.8 %. However, the battery shows a gradual decrease in specific capacity, indicating some capacity fading and discharge capacity reduced to 352.2 mAh/g, which could be attributed to electrode degradation, SEI layer formation, or lithium loss [17]. The large fluctuation (spike) in Coulombic efficiency around cycles 10 to 12 suggests an experimental anomaly, electrolyte instability, or lithium dendrite formation, which could temporarily affect performance [20].

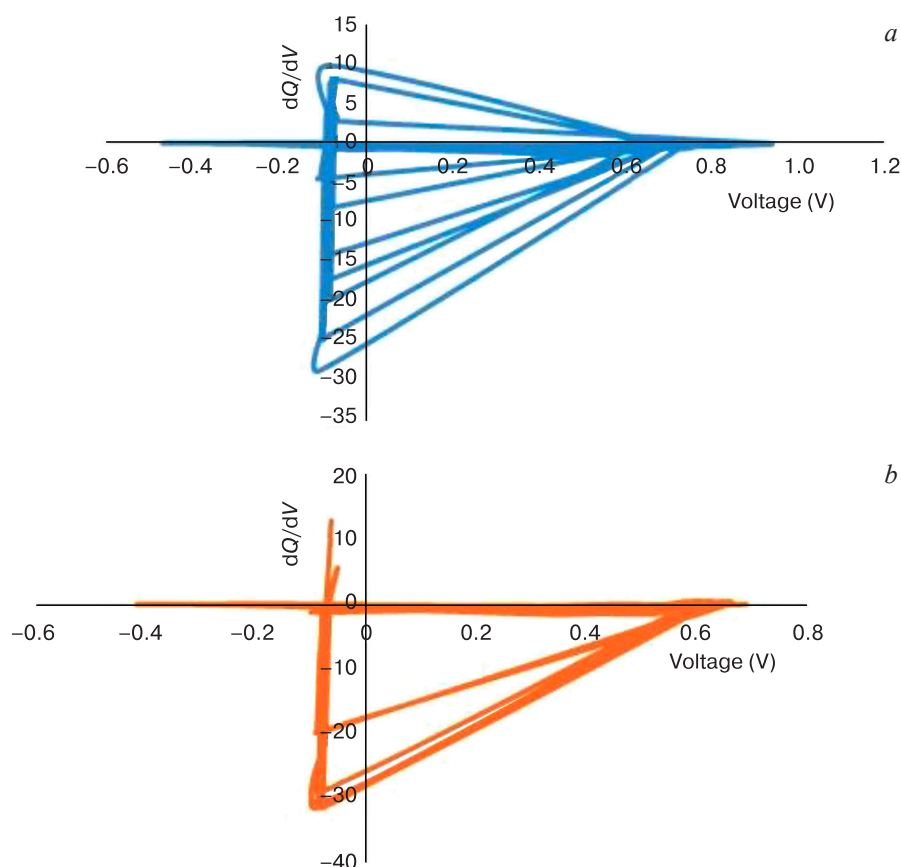


Figure 4. Schematic representation of differential capacity (dQ/dV) vs voltage: (a) fresh cell and (b) after 40 charge-discharge cycles

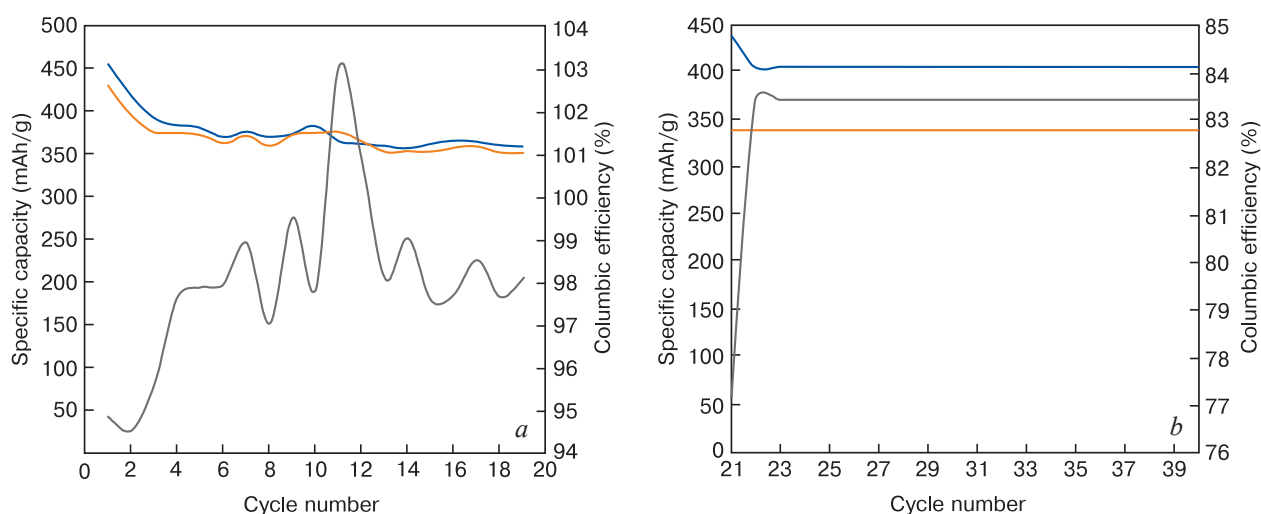


Figure 5. Change of specific capacity and coulombic efficiency during (a) 1–20 and (b) 21–40 charge-discharge cycles at 1C current rating

Figure 5b shows the cycling performance from cycle 21 to cycle 40, focusing on specific capacity and Coulombic efficiency. Here, the blue and orange lines stabilize, suggesting that the battery reaches a more steady-state cycling regime. The Coulombic efficiency improves and remains stable (~82–85 %), meaning that most of the lithium is being effectively cycled, with minimal losses. The charge and discharge capacity at the 21st cycle is observed to be 440.2 mAh/g and 339 mAh/g, respectively.

The discharge capacity was found to be 339 mAh/g at the end of the 40th cycle. The capacity retention appears relatively stable after 40th charge-discharge cycle, however, the gradual decline in Coulombic efficiency suggests ongoing degradation processes such as electrode pulverization, SEI layer thickening, or lithium trapping [20].

Hence, the data suggests that the N350-Cu_xO_y anode experiences initial instability during the first few cycles, likely due to SEI formation and structural changes.

However, after approximately 20 cycles, the system stabilizes, leading to more consistent cycling performance. Despite this stabilization, long-term capacity fading is evident, which is a common challenge in the transition of metal oxide anodes due to their volume expansion and structural degradation.

Conclusion

The experimental investigation of binder-free nanostructured copper oxides (CuO, Cu₂O) as negative electrodes for lithium-ion batteries demonstrates promising electrochemical performance. The material exhibits a high initial charge and discharge capacity of 455.4 and 431.9 mAh/g, respectively, with a Coulombic efficiency of 94.8%. After 40 charge-discharge cycles, the electrodes retain approximately 80% of their initial capacity, maintaining a discharge capacity of 339 mAh/g. These results highlight the potential of nanostructured copper oxides as viable anode materials for lithium-ion batteries,

offering a balance between high capacity and stable cycling performance. Future work should focus on optimizing structural stability and mitigating capacity fading to further enhance long-term performance.

Author contribution

Writing and editing-original draft: Md. Arafat Rahman and Md. Muktadir Billah; experimentation and data curation: Syed Md. Ikram; review & editing: Md. Muktadir Billah and Jesia Alam Jui; fund acquisition: Md. Arafat Rahman.

Conflicts of interest and data availability statement

All authors report no conflict of interest in any part of this study. Provided all Data in the manuscript.

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