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Rechargeable zinc-air battery with bifunctional electrocatalyst of copper oxide and graphene nanoplatelets

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ABSTRACT

Rechargeable zinc-air batteries have been identified as promising technologies for energy storage. However, developing cost-effective electrocatalysts that can efficiently facilitate the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) is crucial for their advancement. This work investigates synthesized electrocatalysts composed of graphene-Cu_2O deposited on carbon cloth by doctor blading casting method as bifunctional electrodes in a rechargeable Zn-air battery. The battery integrated with graphene-Cu_2O as the air-cathode electrocatalyst showed superior performance in terms of cycling stability compared to that without Cu_2O. This enhanced performance is attributed to the reversibility of Cu^{+}/Cu^{2+} species during the redox reactions facilitated by the high electrical conductivity of graphene. Therefore, the results suggest the potential of the synthesized electrodes for advancing the development of rechargeable Zn-air batteries.

1. Introduction

Zinc-air batteries (ZABs) have emerged as promising alternative energy storage technologies due to their safer design, lower cost, and higher theoretical energy density than the current commercialized lithium-ion batteries [1–4]. ZABs consist of zinc and air electrodes separated by an electrolyte, usually an aqueous alkaline solution. These batteries generate electricity through zinc oxidation in the metal electrode, whereas the oxygen reduction reaction (ORR) occurs in the air-electrocatalyst. For rechargeable ZABs (RZABs), opposite reactions occur during charging: the zinc reduction in the metal electrode and the oxygen evolution reaction (OER) in the air electrode. However, RZABs still face issues regarding their cyclability performance, making developing novel electrocatalysts crucial for enhancing their power density, specific capacity, and round efficiency [5–8]. Noble metal-based catalysts such as platinum (Pt) and ruthenium and iridium oxides (RuO_2 and IrO_2) have shown desirable electrocatalytic activities, but their high costs limit the large-scale commercial applications of rechargeable zinc-air batteries. Therefore, efforts have been directed toward investigating electrocatalysts based on earth-abundant elements that aim to achieve high electrocatalytic performance and competitive cost [9–11].

Combining carbon materials with metal oxides is a promising approach for creating cost-efficient materials with enhanced electrocatalytic performances. Carbon-based materials, such as graphene and carbon-black, can increase conductivity and surface area, while metal oxides can improve catalytic activity and potentially reduce costs due to their abundance on Earth. However, finding metal-oxides that can act as bifunctional electrocatalysts for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in RZABs remains challenging. Most studies on metal-oxides as bifunctional air electrodes for RZABs have focused on CoO_x, MnO_x, and FeO_x [12–20]. These metals have incomplete orbitals, allowing electron movement and thus the ORR and OER catalysis. For instance, Co_3O_4 is one of the most investigated metal-oxides for ZABs and promotes the OER through its Co^{2+} species, while the Co^{3+} species can support the ORR [21]. In this regard, CuO_x also appears to be a promising alternative for bifunctional air-electrocatalysts because of its incomplete d-orbital, which allows for easy interconversion between Cu^{+} and Cu^{2+} species. CuO_x has been widely applied in photoelectrochemistry, including photo-electrocatalytic fuel cells and photoelectrocatalytic batteries [22–26].

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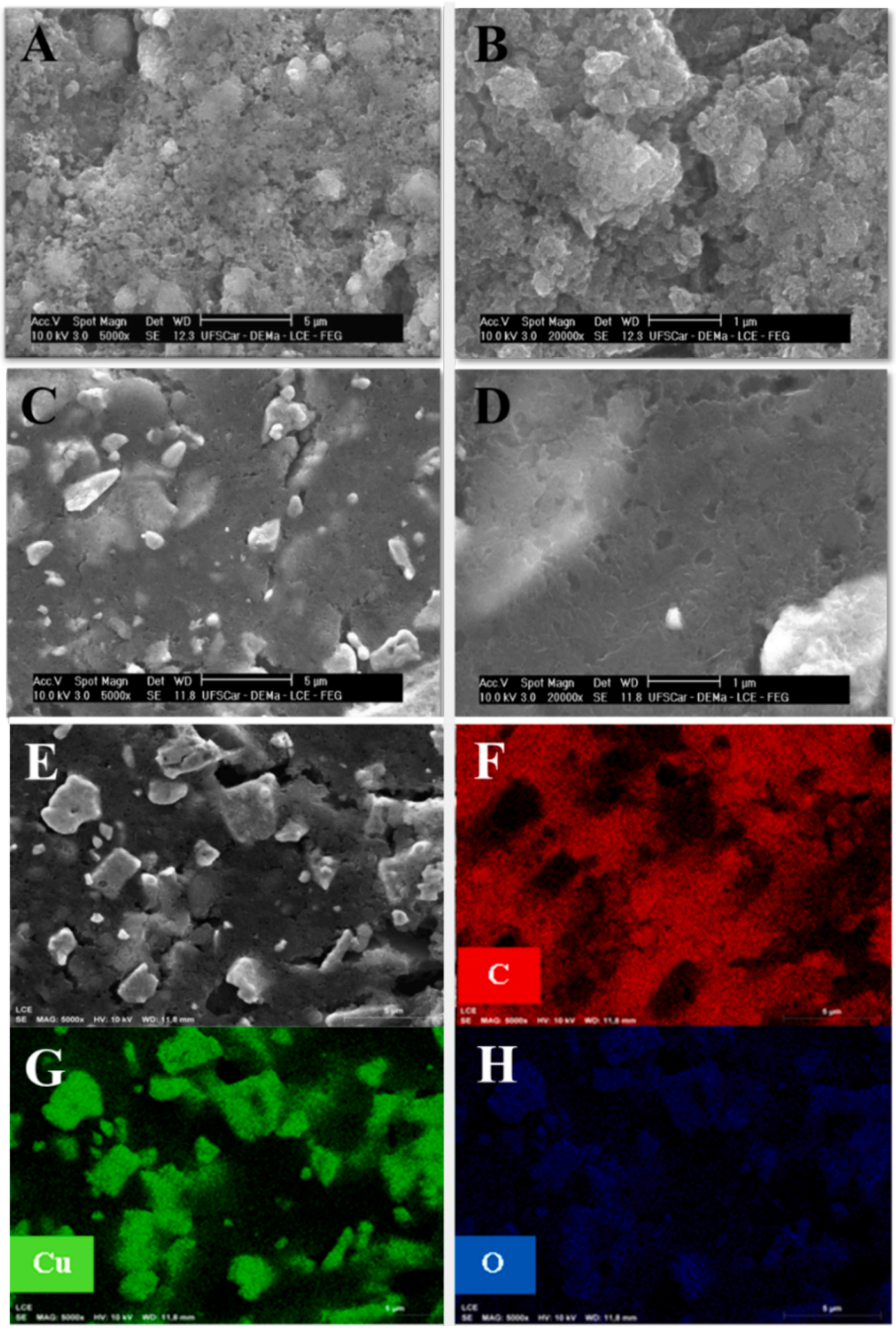

Fig. 1. SEM images of graphene (A, B) and graphene with Cu_2O (C, D) films, and EDS mappings of elements C, Cu, and O for the graphene-Cu_2O film.

However, copper oxides combined with graphene have not yet been reported as a bifunctional air-electrode for RZABs. Thus, this study aims to investigate the potential use of Cu_2O coupled with graphene nanoplatelets as a bifunctional electrocatalyst for OER and ORR in rechargeable Zn-air batteries.

2. Materials and methods

2.1. Electrode synthesis

All materials used were analytical grade and sourced from Sigma Aldrich unless otherwise specified. Carbon cloth (CC) was obtained from Fuel Cell Earth (Wobum, MA, USA). The synthesized electrode was composed of a graphene-based paste, which was deposited on carbon cloth as the electrocatalyst. The graphene-based paste was prepared as reported previously [27]. 1 g of graphene was mixed with 5 mL of distilled water and 0.4 mL polytetrafluorethylene (Teflon 60 % wt. dispersion in water) by vigorous mixing to create a viscous paste. For the paste containing copper oxides, 4 g of Cu_2O was also added. The quantity of Cu_2O used was determined through pre-experiments, which showed slightly better short-circuit current values with this amount, but further increasing it resulted in the paste becoming too viscous to deposit. It was also found that without graphene, the film was not hydrophobic and could not be deposited on the carbon cloth surface. The paste was deposited on the carbon cloth by doctor blade casting using a spatula, and the electrode was annealed in an oven at 340 °C for 15 min in the ambient atmosphere. This procedure was repeated once to ensure that the carbon cloth was completely covered with the carbon layer, resulting in approximately 0.03 g cm^{-2} of dried paste for each electrode.

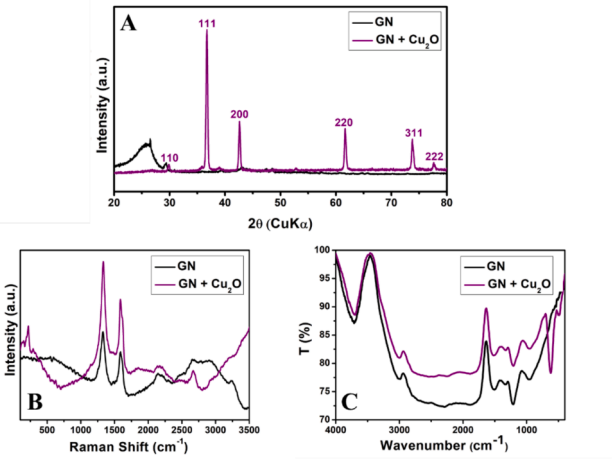

Fig. 2. XRD pattern (A), Raman (B), and FTIR (C) spectra of the samples GN and GN-Cu_2O.

2.2. Structural and morphological characterization

The structural and morphological properties of the electrodes synthesized with and without Cu_2O were investigated by scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), Raman, and infrared spectroscopy. The SEM and EDS examinations were carried out using a tungsten electron source operating at a potential of 10 kV. For SEM, the secondary electron (ES) mode was employed at magnifications of 5000x and 20000x. The XRD measurements were conducted using a 2θ range ranging from 5 to 80°, with a scanning speed of 2° min^{-1}, and Cu Kα radiation (λ = 1.54056 Å) at 30 kV and 30 mA on a Rigaku diffractometer Miniflex 600. Raman spectra were obtained using an Olympus TM BX41 microscope coupled with a Horiba Jobin-Yvon Raman LabRAM micro spectrometer at room temperature with a He-Ne laser line as the excitation source.

2.3. Electrochemical measurements

The electrochemical characterization was conducted using an active area of 1.0 cm^2 on the electrodes in the reactor. The air-electrode side covered with the catalyst was placed in contact with the electrolyte, while the other side was exposed to ambient air, facilitating oxygen entry. Electrochemical characterization was performed using 3 and 2-electrode configurations to assess the performance of the air electrode and the battery performance, respectively. A reference electrode is also used in a 3-electrode characterization, besides the working electrode and the counter electrode. For the 3-electrode configuration, the synthesized electrocatalysts deposited on the carbon cloth were used as the working electrode, while an Ag/AgCl (3 M KCl) electrode served as the reference electrode, and a Pt foil was used as the counter electrode. The electrodes were immersed in a 0.1 M KOH aqueous electrolyte. For the zinc-air battery characterization, the synthesized electrodes (electrocatalysts on the carbon cloth) were used as the air electrode, and a zinc-foil was used as the metal electrode. The measurements were performed

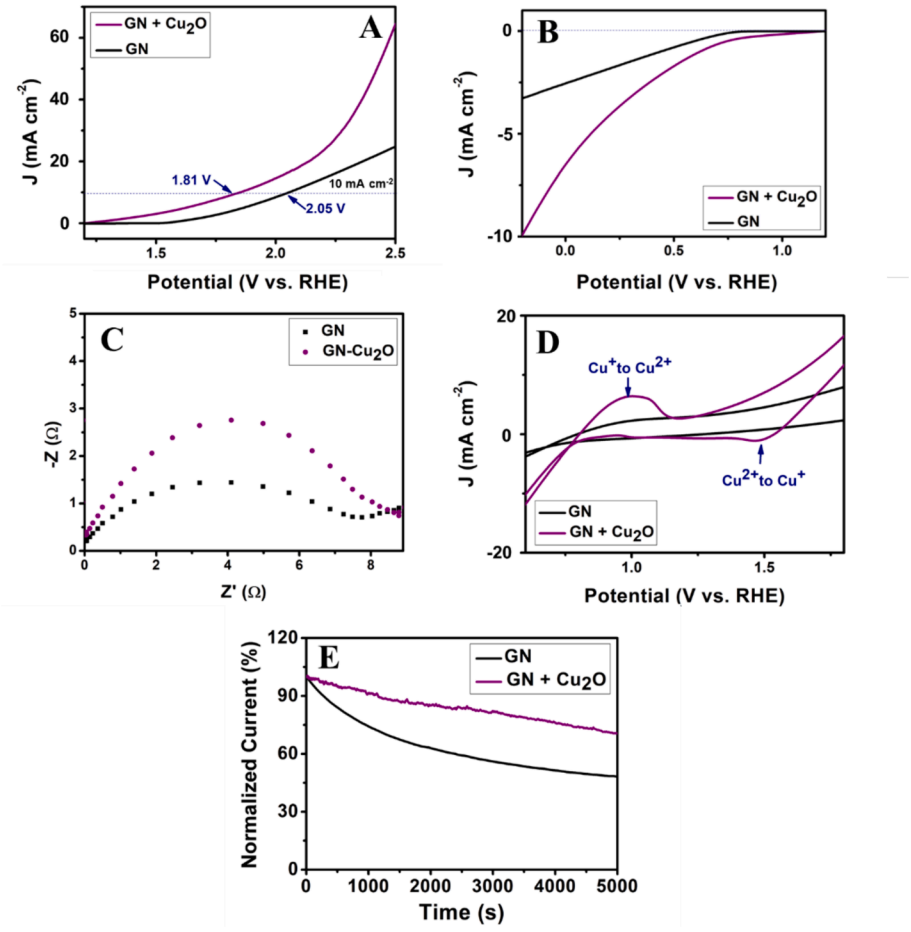

Fig. 3. OER (A) and ORR (B) polarization curves, electrochemical impedance spectroscopy (C) cyclic voltammograms (D), and current–time chronoamperometric responses (E) for GN and GN-Cu_2O electrodes in alkaline media (0.1 M KOH).

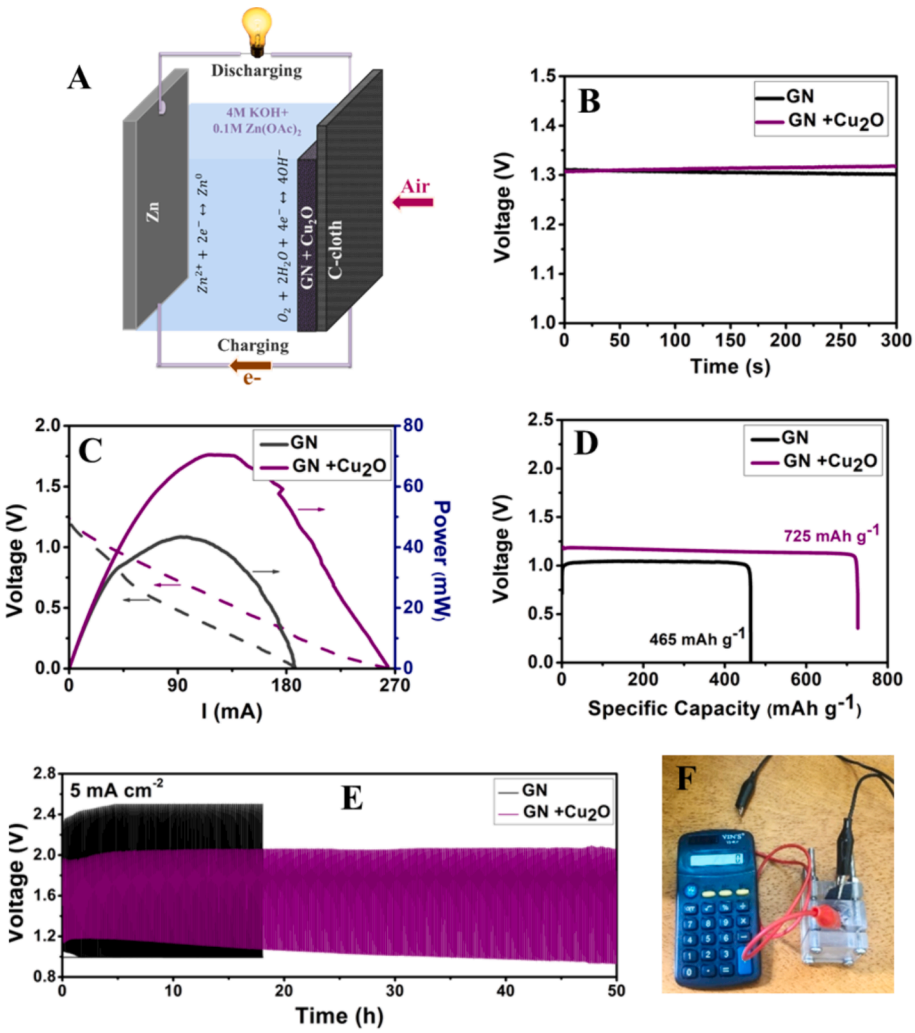

Fig. 4. Rechargeable Zn-air battery schematic representation (A). OCV measurements (B), IV, and power curves (C), specific discharging capacities at 10 mA cm^{-2} (D), and charging-discharging cycles of the batteries composed of GN or GN-Cu_2O electrodes at 300-second cycles, i.e. shallow cycling (E). Demonstration of the constructed battery connected to a calculator (F).

in a one-compartment plexiglass reactor filled with 4 M aqueous KOH and 0.1 M $Zn(CH_3COO)_2$.

3. Results and discussion

3.1. Structural and morphological electrode characterization

SEM images of the graphene electrode without Cu_2O particles revealed a porous, sponge-like structure, as shown in Fig. 1A-B. Conversely, adding Cu_2O particles resulted in a more rigid morphology with nanometric clusters, which clearly indicated the Cu_2O incorporation onto graphene support, as shown in Fig. 1C-D. The EDS mapping images of the GN-Cu_2O film confirmed the distribution of carbon (C) throughout the surface and the filling of gaps by oxygen (O) and copper (Cu) atoms, as seen in Fig. 1F-H.

The X-ray diffraction analysis of the GN-Cu_2O electrode revealed the cubic crystalline phase of Cu_2O (JCPDS #05-0667) identified by its Miller indices of (110), (111), (200), (220), (311), and (222) (Fig. 2A). Conversely, no crystalline phase is detected in the GN electrode. The Raman spectra of the graphene film showed D and G bands at 1333 and 1586 cm^{-1}, respectively, with the intensity ratio (ID/IG) of the two bands indicating graphene defect. Adding Cu_2O particles increases the disorder, i.e. ID/IG from 1.06 to 1.11, and the oxygen-containing groups, as seen in Fig. 2B [28–31]. The Raman shift at 635 cm^{-1} can be associated with the presence of Cu_2O in the carbon structure [30,32]. The FTIR spectra (Fig. 2C), revealed a band at 620 cm^{-1} for GN-Cu_2O, characteristic of the Cu–O vibration. The other bands in both samples can be attributed to the vibration of C═C bonds in the carbon network at 1578 cm^{-1} and the weak O–H vibration at 3450 cm^{-1} [31,33].

3.2. Electrochemical activities

The findings from the electrochemical characterization demonstrated that modifying the air-electrode with GN-Cu_2O electrocatalyst had a positive impact on the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), suggesting that GN-Cu_2O could be applied as a bifunctional electrocatalyst for RZABs. The linear voltammogram (Fig. 3A) revealed a decrease in the onset potential for the OER, from 2.05 V using the GN electrode to 1.81 V vs. RHE using the GN-Cu_2O. Additionally, the ORR activity is poor with $E_{1/2}$ close to zero for the GN electrocatalyst and about 0.25 V vs. RHE for the GN-Cu_2O (Fig. 3B). These results indicate that the GN-Cu_2O electrode can improve battery discharging and charging, making it a promising candidate for bifunctional electrodes. The electrochemical impedance spectroscopy (EIS) revealed similar charger transfer resistance to the electrocatalyst of GN-Cu_2O compared to the GN electrocatalyst (R_{CT}-GN-Cu_2O = 8.5 Ω and R_{CT}-GN = 8.0 Ω), as shown in Fig. 3C. Nevertheless, the higher catalytic activity of the GN-Cu_2O electrode can be attributed to the reversibility

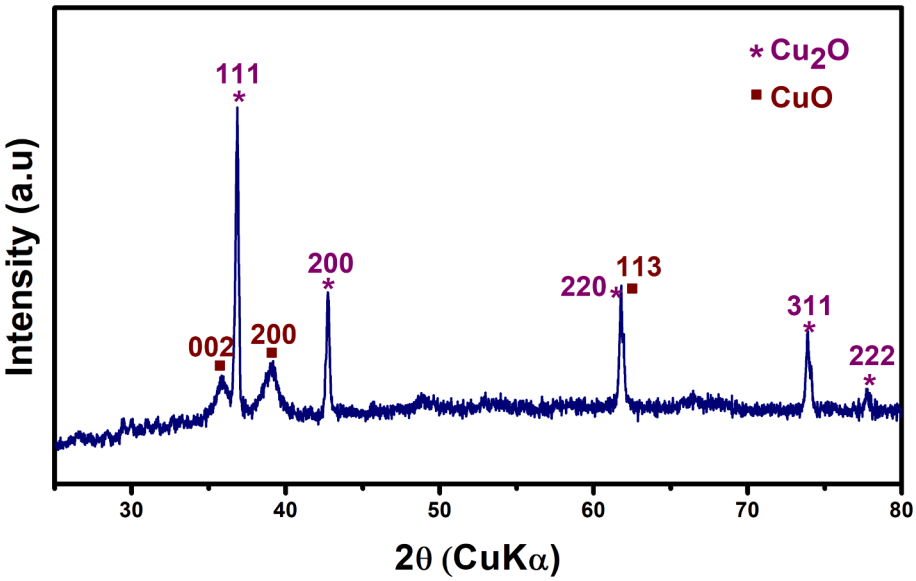

Fig. 5. XRD pattern for the electrocatalyst GN-Cu_2O after the battery operation.

between Cu^{2+} and Cu^{+} ions, as identified in the cyclic voltammogram shown in Fig. 3D. This switch in the Cu ions has also been observed in recent investigations of novel electrocatalysts for Zn-air batteries, but only under lighting or coupled with Co_3O_4 [22,34]. In this work, the high conductivity of graphene is associated with the promotion of Cu speciation. Therefore, the double oxidation state of Cu ions generated at the OER and ORR potentials should boost the catalysis of redox reactions during battery operation. Furthermore, the stability test of the electrode at a constant potential of −0.6 V vs. Ag/AgCl (Fig. 3D) demonstrated the superior performance of the GN-Cu_2O electrode, with over 70 % of its original current remaining after several hours, confirming its potential for use in rechargeable Zn-air batteries.

3.3. Rechargeable zinc-air batteries

To assess the functionality of the rechargeable Zn-air battery electrodes, we implemented and tested the scheme depicted in Fig. 4A using either the GN or the GN-Cu_2O sample as the electrocatalyst deposited on carbon cloth. The results showed similar open-circuit voltages (OCV) of approximately 1.3 V for both batteries (Fig. 4B). This agrees with previous results that show that the practical OCVs of Zn-air batteries are lower than the theoretical 1.6 due to overpotential losses. However, the short-circuit current and power density of the battery with the GN-Cu_2O electrocatalyst were significantly higher than those without Cu_2O in the air-electrode. The values of the short-circuit current and power density ranged from 190 to 260 mA and 42 to 75 mW, respectively, as shown in Fig. 4C. Other studies that use metal oxides, e.g., Co_3O_4, $NiCo_2O_4$, with graphene have reported power density in the range of 50–200 mW cm^{-2}. The relative increase in power density compared to the reference sample used in those studies was in the range of 50–56 %. Meanwhile, in this work, the relative increase was about 78 %, demonstrating the positive effect of the Cu_2O on the battery performance [35–38]. The battery with the GN-Cu_2O electrocatalyst also had a higher specific capacity of 725 mAh g^{-1} at a continuous current of 10 mA, as compared to 465 mAh g^{-1} for the battery without Cu_2O (Fig. 4D). The relative improvement shown to the specific capacity provided by the Cu_2O was also more significant than other reported metal oxides combined with graphene [35–38]. Further, the charge–discharge stability test demonstrated the potential of the GN-Cu_2O for use as a bifunctional electrocatalyst in RZABs, with a lower voltage change for charge and discharge potentials, consistently with experimental findings shown in Fig. 3A-B, as well as a superior cyclability The battery with the GN-Cu_2O electrode remained stable for 50 h, as shown in Fig. 4E. Finally, the practical applicability of the battery is demonstrated by connecting it to a calculator, as shown in Fig. 4F. After the battery application, the XRD pattern for the electrocatalyst has revealed both Cu_2O and CuO phases, as shown in Fig. 5, supporting the existence of the redox couple Cu^{+} and Cu^{2+} during the operation. Table 1 presents the performance of reported ZABs that used electrocatalysts composed of graphene/carbon-based materials, or/and Cu_2O or other metal oxides.

Table 1

Electrocatalyst	Peak power density (*)	Specific capacity (*)	Reference
Graphene-Cu_2O	75 mW cm^{-2} (78 %)	725 mAh g^{-1} (56 %)	This work
ZnO/Cu_2O	8 mW cm^{-2} (85 %)	334 mAh g^{-1} (–)	[22]
Ccube/Cu_2O/Co_3O_4	219 mW cm^{-2} (15 %)	781 mAh g^{-1} (–)	[34]
rGO/$NiCo_2O_4$	125 mW cm^{-2} (26 %)	720 mAh g^{-1} (–)	[35]
rGO-Co@Co_3O_4/FeNS	181 mW cm^{-2} (51 %)	–	[36]
N-rGO/Co_3O_4	47 mW cm^{-2} (56 %)	875 mAh g^{-1} (15 %)	[37]
N-graphene/CoO	135 mW cm^{-2} (48 %)	815 mAh g^{-1} (4 %)	[38]
Cnanotube-Co_3O_4	267 mW cm^{-2} (5 %)	814 mAh g^{-1} (3 %)	[39]
Cspheres/Mn_3O_4	183 mW cm^{-2} (16 %)	–	[40]
Cnanotube/ Mn_3O_4	87 mW cm^{-2} (18 %)	823 mAh g^{-1} (–)	[41]
MnO_x/CC	148 mW cm^{-2} (17 %)	816 mAh g^{-1} (–)	[42]
Fe_3O_4/N-C nanoflower	137 mW cm^{-2} (42 %)	749 mAh g^{-1} (11 %)	[43]
Fe_3O_4/N-carbon spheres	141 mW cm^{-2} (64 %)	723 mAh g^{-1} (11 %)	[44]

* Increase relative to reference sample.

4. Conclusion

In this work, we investigated the potential of a bifunctional electrode composed of Cu_2O and graphene for use in a rechargeable zinc-air battery. Electrochemical characterization showed that the electrode could carry out both the OER and ORR due to the reversibility of Cu^{+}/Cu^{2+} ions within the redox voltage range. When applied to the

rechargeable Zn-air battery, the device demonstrated higher power, specific capacity, and stability than batteries without the Cu_2O component. Therefore, this study highlights the potential of graphene-Cu_2O electrocatalysts for use in rechargeable Zn-air batteries, which could contribute to the advancement of such technologies.

CRediT authorship contribution statement

Barbara A.C. Sá: Writing – review & editing, Methodology, Investigation. **Tatiana S. Andrade:** Writing – original draft, Supervision, Conceptualization. **Rafael R. de Souza:** Writing – review & editing, Investigation. **Antero R. Santos Neto:** Writing – review & editing. **Mariandry Rodriguez:** Writing – review & editing. **Francisco G.E. Nogueira:** Writing – review & editing, Resources. **Márcio C. Pereira:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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