



An Alternative Aluminum-copper Galvanic Cell Model for Aluminum Ion Battery Systems Using CuO Nanoparticles in Acidic Mixture Electrolyte

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ABSTRACT

A Novel Al-Cu galvanic cell in high chloride acidic aqueous electrolyte has been developed as an alternative to already existing aluminum ion battery systems. An acid electrolyte aqueous system with 3% NaCl and 1000 ppm CuO NPs (synthesized by chemical precipitation) was chosen, and the performance of the galvanic cell was evaluated by measuring its internal electrolytic resistance, specific capacity, and cell potential. These cell parameters were then compared with unmixed and uncharged CuO NPs electrolytic systems. When compared to a system without CuO NPs system, a single pair system with CuO NPs shows a 6.6-time drop in electrolytic resistance, while for three-pair cell charged system connected in series shows a maximum cell potential of 1610 mV and a 1.94-time decrease in electrolytic resistance. The presence of CuO NPs in the electrolyte and its cathodic depolarization effect (decrease of hydrogen overvoltage and stabilization of the electrolyte), are responsible for the improvement in cell performance for both single and three-pair systems.

Keywords: Galvanic cell; Electrolyte; CuO nanoparticles; Cell potential; Capacity; Cathodic depolarizer.

1. INTRODUCTION

Aluminum's abundance, low cost, and high theoretical capacity from its three-electron redox mechanism make aluminum-ion batteries (AIBs) a possible substitute for lithium-ion batteries. Decades of research have been conducted, with the most recent developments concentrating on electrolytes and cathodes to enhance the performance of batteries. Targeting high volumetric capacity of aluminum, early AIB research started in the 1970s but encountered problems with oxide layer production in aqueous electrolytes. The use of non-aqueous chloroaluminate ionic liquids for reversible plating sped up development in the 1980s, but cathode constraints halted progress in the face of lithium-ion dominance and the energy density of aluminum batteries was also hindered by low capacity. Aqueous and non-aqueous electrolytic systems for AIBs (Shyamal *et al.* 2017; Amit *et al.* 2024; Di-Yan *et al.* 2017; Michael *et al.* 2017; Lin *et al.* 2015; Sandeep *et al.* 2021; Bei *et al.* 2022; Jiajin *et al.* 2025) have been developed in recent years using various types of cathodes in an effort to meet out the energy demands of electric vehicles in a way that is both economical and pollution-free. Like lithium and emerging sodium ion batteries, aluminum ion batteries are classified as high energy density batteries. Compared to a Li-ion battery, AIB delivers three electrons from the active aluminum

ion. Its main benefits are affordability and abundance of Al in the earth's crust.

Aluminum as an anode active material is reported to have two main drawbacks. Firstly, the formation of the passivation layer, which reduces the operating cell voltage and increases the charge transfer and the bulk transfer resistance (i.e., internal resistance) leading to a drop in the open circuit potential of the Al anode from -2.34 V (Nernst equation value) to -1.8 V vs SHE at pH above 10, which limits the operating cell voltage and expected energy density. On the other hand, at low pH, the possibility of corrosion of the anode aluminum leads to a drop in cell voltage between 1.2 - 1.6 V. The fundamental issue in aqueous systems is the accumulation of H₂ gas (hydrogen overvoltage) or the reduction of dissolved oxygen at the cathode (Ehsan *et al.* 2021).

When used as battery electrode, Al can undergo an electrochemical reaction of three-electron transfer. Among many metal anodes, the theoretical mass specific capacity of aluminum is second only to lithium (2980 mA h/g for Al, 3860 mA h/g for Li), and the volume specific capacity is nearly 4 times that of lithium (8040 mA h/cm³ for Al, 2062 mA h/cm³ for Li). (Tan *et al.* 2022; Huicong *et al.* 2019; Qingfeng and Niels, 2002). CuO acts as a conversion cathode (CuO + Al³⁺ → intermediates → Cu/Al₂O₃-like phases),

reducing polarization losses and overcoming anode passivation (Zulai Cao *et al.* 2023).

In this study, we built a unique Al ion battery with a Cu cathode, and an Al anode, and three electrolyte compositions using HCl, NaCl, and CuO NPs (cathodic depolarizer) to improve overall cell efficiency in an aqueous environment as shown in Table 1.

2. EXPERIMENTAL WORK

2.1 Synthesis of Copper (II) Oxide Nanoparticles

Table 1. Details of electrolytes used in Al-Cu galvanic cell

S. No.	Electrolyte	Composition of Electrolytes
1.	Acid mixture	1.5 M HCl dissolved in 100 mL of double-distilled water.
2.	Acid mixture + 3% NaCl	1.5 M HCl dissolved in 100 mL of double-distilled water, to which 3 g of NaCl is added.
3	Acid mixture + 3% NaCl+ 1000 ppm CuO NPs	1.5 M HCl dissolved in 100 mL of double-distilled water + 3 g of NaCl + 100 mg CuO NPs

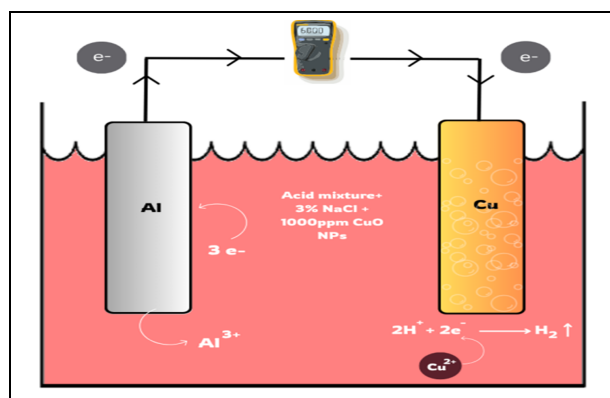


Fig. 1: Graphical diagram of aluminum ion galvanic cell system using CuO as cathodic depolariser

Copper (II) oxide nanoparticles were synthesized by the chemical precipitation method, which involves adding 200 mL of distilled water, 1.02 g of CuCl_2 , and 4 g of NaOH to a 500 mL beaker containing copper chloride precipitate in an alkaline medium. After that, the mixture was heated to 80°C for three hours duration using a magnetic stirrer in a thermostat. After adding HCl to neutralize the precipitate, it changes from a blue to a black precipitate. Following filtration and purification by ethanol, it was rinsed with double-distilled water and dried for two hours at 120°C in an oven and then finally copper(II) oxide nanoparticles were collected. We employed the as-synthesised CuO NPs as a cathodic depolarizer in an acidic mixed electrolyte to increase the cell efficiency in the Al-Cu galvanic cell under investigation.

2.2 Experimental Set Up of an Aluminum ion Galvanic Cell System

Aluminum Anode: With a weight of 2.49 g (1 mm thick) and an exposure area of 8 cm^2 , pure aluminum serves as the anode in this Aluminum ion Galvanic cell system with high acidic environment ($\text{pH} < 2$).

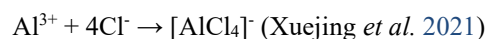
Copper Cathode: Pure copper serves as the cathode with a weight of 29.18 g (2 mm thick) and an exposure area of 8 cm^2 .

Electrolyte: The electrolyte consists of three different compositions of acidic mixture. Al foil weighing 0.311 g ($1 \times 1\text{ cm}^2$) area treated in 1.5 M of HCl solution in 100 mL of double-distilled water creates half-cell for the electrode-electrolyte interface of battery system. The experimental setup of the AIB system consists of Cu as the cathode and Al as the anode in different electrolyte mixtures.

2.3 Mechanism of Cell Reaction in Aluminium ion Galvanic Cell

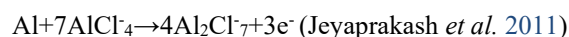
Fig. 1 shows the proposed AIB system. Here, the formation of $\text{Al}(\text{OH})_3$ is unlikely and the chloride ions are crucial for maintaining ionic flow. The formation of $[\text{AlCl}_4]^-$ complex ensures the continuous operation of the battery.

At high chloride concentration, possibility of complex formation are;



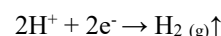
The most common redox reaction in aluminum battery is;

At the Anode;



At the cathode;

Here, copper acts as a surface for completing the circuit by accepting the electron and thus favoring hydrogen evolution



The theoretical capacity of these systems has been significantly affected by the fact that AIBs really require 8 Al atoms per 3 electrons rather than 1 Al atom per 3 electrons. Therefore, rather than the widely cited 2980 mAh/g, the theoretical capacity of the anode reaction is really 67 mAh/g.

$$C_{\text{theoretical}} = nF / [3.6 \times (M_{\text{Al}} + 7M_{\text{AlCl}_4^-})]$$

3. RESULTS AND DISCUSSION

3.1 PXRD Pattern of CuO NPs

Fig. 2 shows the Powder X-ray Diffraction (PXRD) pattern of CuO nanoparticles. The spectrum exhibits multiple sharp and intense peaks, indicating good crystallinity of the CuO nanoparticles. The highest intensity peak appears near $2\theta \approx 35.5^\circ$, which corresponds to the (210/-111) plane of CuO, suggesting it may be the preferred orientation. The peaks match well with the standard monoclinic phase of cupric oxide (CuO) (JCPDS card no: 45-0937), confirming the successful formation of CuO. The crystal size was found through Scherrer equation and the average is 36.62 nm.

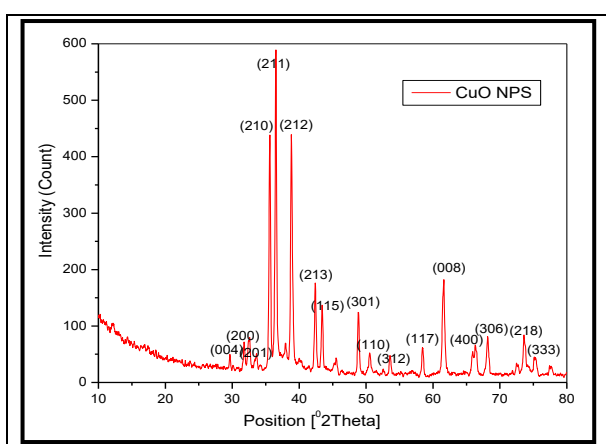


Fig. 2: PXRD pattern of synthesized CuO nanoparticles

3.2 Electronic Spectral Analysis of CuO NPs

Fig. 3 shows the UV-Visible spectrum of the synthesized CuO NPs. The formation of CuO nanoparticles was confirmed by the observation of the band between 275 and 400 nm.

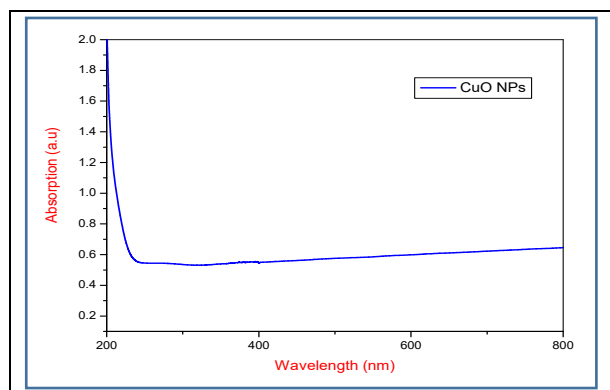


Fig. 3: UV-visible spectrum of synthesized CuO NPs

3.3 FTIR Spectrum of CuO Nanoparticle

Fig. 4 represents the FTIR spectrum of CuO NPs. It exhibits numerous major absorption peaks

corresponding to various functional groups and bonding vibrations. The large peak of 3400 cm^{-1} was assigned to O-H stretching vibration, whereas the peak at 2920 cm^{-1} was attributed to C-H stretching vibration. These might have arisen from the residues of capping agents or synthesis precursors. The peaks around $\sim 1600\text{ cm}^{-1}$ are due to C=O stretching, indicating carbonyl molecules from precursors. Strong peaks in the range $\sim 500\text{--}600\text{ cm}^{-1}$ confirm the existence of copper oxide nanoparticles (Dagher *et al.* 2014; Saif *et al.* 2021).

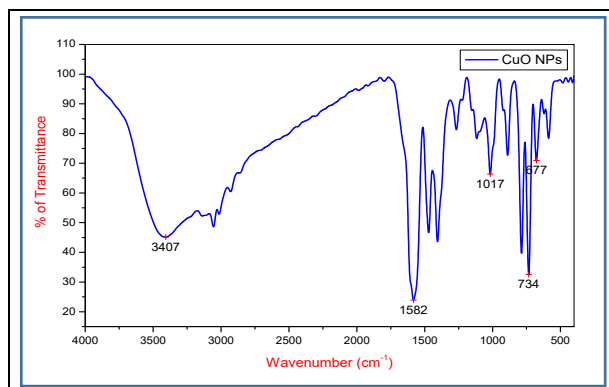


Fig. 4: FTIR spectrum of synthesized CuO nanoparticles

3.4 SEM Images of CuO NPs

The SEM image is shown in Fig. 5. The particle diameters of CuO NPs range from 190 to 295 nm. The morphology is inconsistent to semi-spherical with some agglomeration. This data supports the nanoscale qualities required for catalytic, sensor, and energy storage applications.

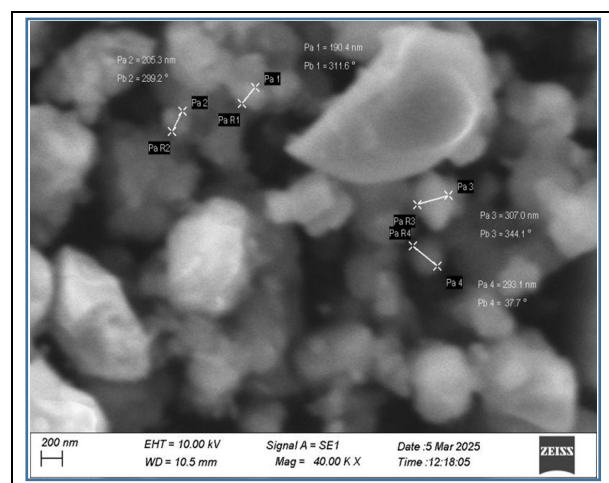


Fig. 5: SEM image of synthesized copper(II) oxide nanoparticles used as cathodic depolariser in Al-ion galvanic cell

The cell potential (mV) vs. time (min) curves for three distinct hydrochloric acid mixed electrolytic systems a) acid mixture, b) acid mixture + 3% NaCl, and c) acid mixture + 3% NaCl + 1000 ppm CuO are

shown in Fig. 6. It is observed that the potential of the HCl alone electrolytic system is unstable. In contrast, systems b and c show stable potential curves, which are caused by the increased conductance in the presence of a high chloride content. When comparing the three systems, system b attained the maximum cell voltage of a 580 mV. In each case, the electrolytic internal resistance of this galvanic cell was the cause of the potential drop as expected from theoretical Nernstian potential (2.0 V).

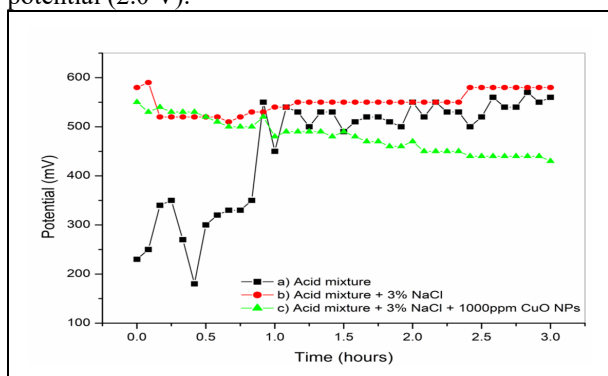


Fig. 6: Potential (mV) vs. time (min) curves

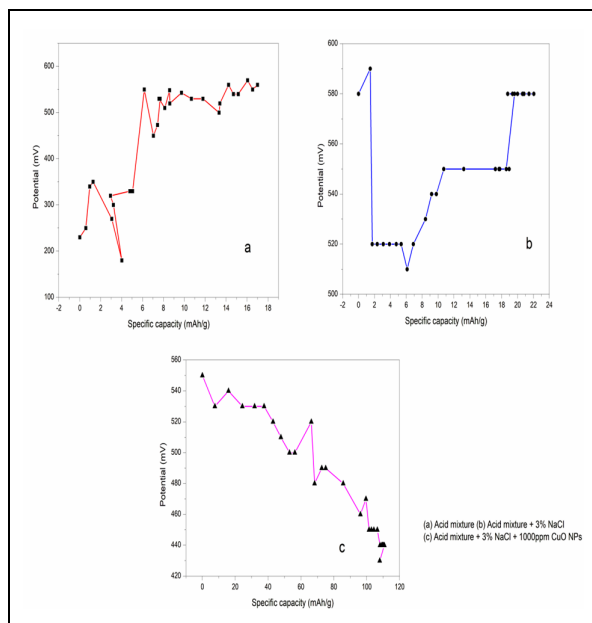


Fig. 7: Potential (mV) vs. specific capacity (mAh/g)

Fig. 7 represents the Potential (mV) vs. Specific capacity (mAh/g) graphs of different electrolytic cell systems with a copper cathode and an aluminum anode. From this figure, it is observed that system b attains the maximum capacity of 22 mAh/g with stable rise in capacity due to the presence of NaCl which maintains the ionic conductivity. The formation of $[AlCl_4]^-$ as an intermediate complex in presence of high concentration of chloride and Al^{3+} ions is assumed to be the cause of the stable increase in capacity of cases a and b. Although the addition of a cathodic depolarizer

CuO in system c will decrease the hydrogen evolution reaction and increase the cell capacity up to 140mAh/g, the cathodic hydrogen evolution reaction will slow down, which will result in a decrease in potential with respect to cell capacity.

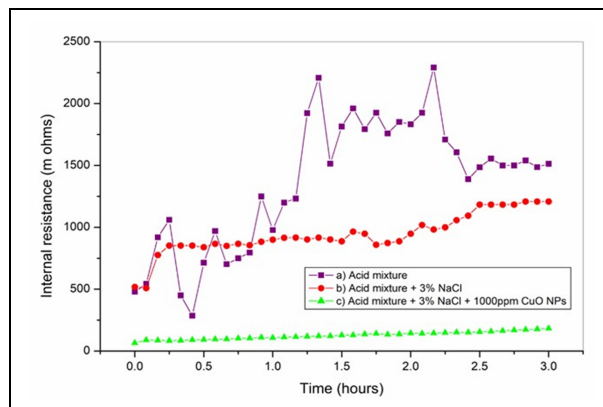


Fig. 8: Time (hours) vs. internal resistance (mohms) graph

The time (hours) vs. internal resistance (m ohms) graphs for the AIBs are shown in Fig. 8. According to this graph, an Al galvanic cell with an aqueous electrolyte of $AlCl_3$ has low electrolytic resistance due to its high ionic conductivity, but has a lot of side reactions that reduce cell efficiency. For example, system a has an acid mixture with a higher internal electrolytic resistance of 1513 mohms, whereas for system b, it was 1208 mohms, which is 1.25-times decrease compared to system a. On the other hand, a significant decrease of 8.31 times and 6.61 times was noted for system c in comparison to system a and system b, respectively, due to the cathodic depolarisation of CuO NPs.

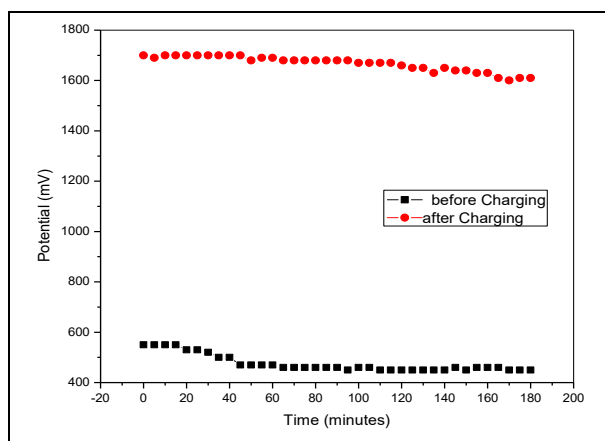


Fig. 9: Potential vs. time study

The potential *versus* time curves for the Al-Cu galvanic cell are shown in Fig. 9. before and after charging. The charging was carried out for one hour using a 9 V primary battery. CuO NPs play a more important role in stabilizing the electrolyte and reducing

hydrogen evolution reaction at the cathode, and inhibit passivation of aluminum at the anode which raises the chemical potential difference between the electrodes after charging, as evidenced by a 3.6-fold increase in potential.

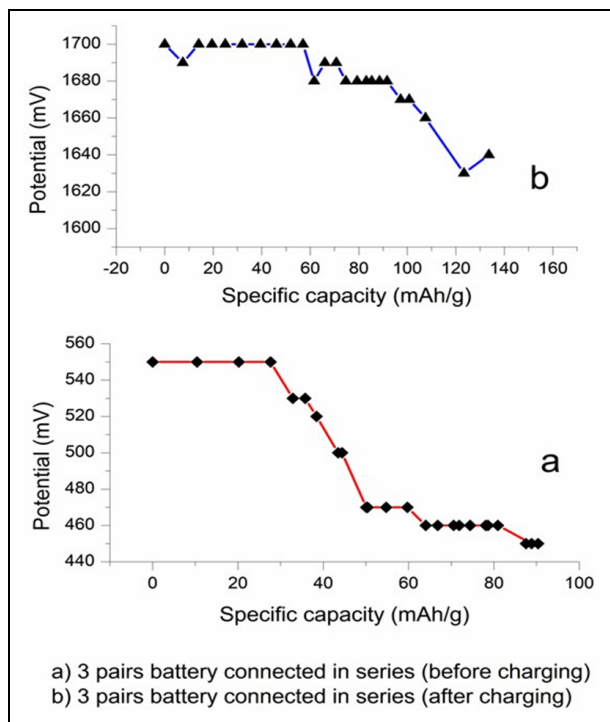


Fig.10: Potential *versus* specific capacity

The potential *versus* specific capacity profiles for the Al-Cu galvanic cell series are shown in Fig. 10. before and after charging. The charging was carried out for one hour using a 9 V primary battery. The greater chemical potential difference produced by the movement of electrons and ions during charging is the reason behind the potential rise after charging aluminum-copper batteries. Since holding more charge (having a greater specific capacity) raises the voltage, this process is directly related to specific capacity. The capacity of the after-charging system is 1.5 times more than that of the before-charging systems, and we have achieved 140 mAh/g.

The internal resistance *versus* time profiles are shown in Fig. 11 before and after charging. The charging was carried out for one hour using a 9 V primary battery. Internal resistance is minimized in an Al-Cu galvanic cell with a three-pair series connected system in a high chloride acid electrolyte because $[\text{AlCl}_4]^-$ and $[\text{Al}_2\text{Cl}_7]^-$ are dominant ionic species rather than free Al^{3+} ions. In contrast, a slight increase in electrolytic resistance occurs in an after-charged Al-Cu three-pair series connected system because of the corresponding increase in cell potential.

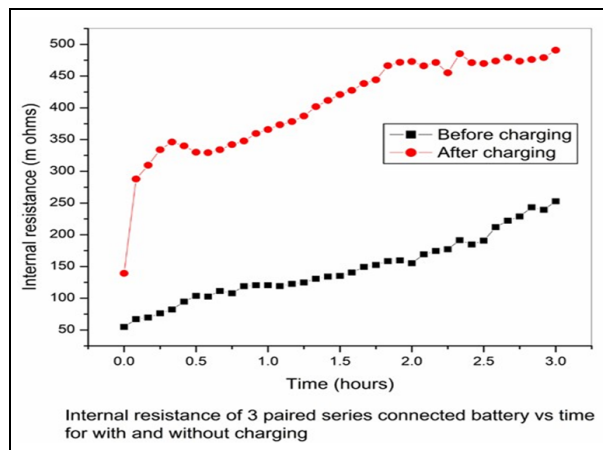


Fig. 11: Internal resistance *vs.* time graphs

4. CONCLUSION

The inclusion of 1000 ppm CuO NPs in the electrolyte increases the cell potential and decreases the internal electrolytic resistance of a three-pair series-connected system both before and after charging. The main factor causing the stable electrolyte with enhanced cell performance for the system is the slowdown of the H_2 evolution reaction at the cathode, which will also slow down the dissolution of Al and stabilize the electrolyte. Three pairs of Al-Cu galvanic cells may achieve a maximum cell capacity of 140 mAh/g as a result, and the cell voltage increased by 3.5 times when compared to before charging. Cell capacity is increased by 4.9 times compared to systems without CuO.

Internal electrolytic resistance was 6.6 times lower in single pair cell systems with CuO NPs than in systems without it. Thus, we have attained a maximum capacity of 150 mAh/g, a cell potential of 1610 mV, and a 1.94-fold reduction in internal electrolytic resistance for charged three-pair cell systems compared to uncharged three-pair cell systems connected in series.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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