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# Challenging metal-ion rocking-chair and zinc-ion mechanisms in mild acidic to neutral aqueous electrolytes

Arvinder Singh<sup>a</sup>, David Grenz<sup>b</sup>, Yann Pellegrin<sup>b</sup>, Fabrice Odobel<sup>b</sup>, Philippe Poizot<sup>a,\*</sup>, Joël Gaubicher<sup>a,\*</sup>

<sup>a</sup> Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, Nantes F-44000, France

<sup>b</sup> Université de Nantes, CNRS, CEISAM, F-44000 Nantes, France

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## ABSTRACT

The utilization of 2,5-ditertbutyl hydroquinone (DTBHQ) as a potential active material in aqueous zinc-ion batteries (AZIBs) was studied for the first time. Thanks to its two hydrophobic groups, DTBHQ demonstrates a maximum solubility of 629  $\mu\text{M/L}$ , significantly lower than that of other reported small quinone derivatives for AZIBs. This property translates to remarkable long-term capacity retention, even at a high electrolyte to active mass ratio. Significantly, our findings provide unequivocal support for a proton insertion mechanism as the main electrochemical process in the solid state in mono- and divalent aqueous electrolytes, thereby challenging the prevailing notion of metal-ion rocking-chair and zinc-ion mechanisms widely reported for aqueous batteries. This novel insight that holds for electrolytes based on metal- ( $\text{K}^+$ ,  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$ ) and non-metal cations ( $\text{NH}_4^+$  and  $\text{NH}_3\text{OH}^+$ ) has profound implications for the understanding and development of aqueous batteries since the operating reduction potential was found to be directly proportional to the  $\text{pK}_a$  values of the predominant acid/base couple of the tested aqueous electrolytes.

## 1. Introduction

Electrochemical energy storage, such as ion insertion batteries, is vital for stabilizing the electricity system in a carbon-neutral future. In this regard, reversible aqueous zinc-ion batteries [1] (AZIB) offer high safety and the potential for cost-effective manufacturing techniques. Organic materials such as quinone derivatives are considered promising candidates for aqueous batteries [2], particularly AZIBs [3] since 1972 [4]. The most reported mechanism in mildly acidic electrolytes is based on the redox-active carbonyl/enolate moiety, along with the insertion/removal of zinc cations to maintain charge balance [3,5–11]. However, a recent study suggests the co-intercalation of protons with  $\text{Zn}^{2+}$  cations [12]. Moreover for AZIBs based on inorganic electroactive materials, an increasing number of studies propose that protons issued from acidic  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  complex rather than  $\text{Zn}^{2+}$  cations, play a critical role in achieving charge neutrality in mildly acidic electrolytes [13,14]. Given the multitude of mechanistic proposals, often conflicting, our objective in this study was to elucidate the reversible charge storage mechanism that occurs in 2,5-ditertbutyl hydroquinone (DTBHQ). The latter was selected for its very low solubility in aqueous electrolytes and

electrochemically assessed vs. monovalent ( $\text{K}^+$ ,  $\text{NH}_3\text{OH}^+$ ,  $\text{NH}_4^+$ ), and divalent cations ( $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ). Our findings provide unequivocal support for a proton insertion mechanism in all tested electrolytes, thus challenging the prevailing notion metal ion rocking-chair and zinc-ion mechanisms predominantly reported in organic-based aqueous batteries.

## 2. Experimental

2,5-Di-*tert*-butylhydroquinone (DTBHQ) were purchased from Aldrich (99 %) and used without further purification. UV-Vis Spectroelectrochemistry of DTBHQ was conducted using a BUNDLE-FLAME-ABS Ocean Optics spectrometer within a glove box (MBraun) under Ar with less than 1 ppm  $\text{O}_2$ . The composite electrode composition was 70 wt% active material, 25 wt% carbon black (Ketjenblack EC-600JD, AkzoNobel), and 5 wt% PTFE. (Full)Half-cell cycling tests were performed using a (zinc foil) threefold oversized activated carbon counter-electrode whereas cyclic voltammetry measurements (CVs) used platinum wire as the counter electrode and  $\text{AgCl/Ag}$  (sat. KCl,  $E_{\text{eq}} = 0.197$  vs SHE) as the reference electrode. Electrochemical measurements were

\* Corresponding authors.

E-mail addresses: [Philippe.Poizot@cnsr-immn.fr](mailto:Philippe.Poizot@cnsr-immn.fr) (P. Poizot), [Joel.Gaubicher@cnsr-immn.fr](mailto:Joel.Gaubicher@cnsr-immn.fr) (J. Gaubicher).

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performed by using a MPG system (Bio-Logic S.A., Seyssinet-Pariset, France) within a glove box under Ar with less than 1 ppm O<sub>2</sub>.

### 3. Results

Considering the primary challenge associated with the use of quinone derivatives in aqueous zinc-ion batteries is their solubility, we specifically employed a commercially available small molecule, namely 2,5-Di-*tert*-butylhydroquinone (DTBHQ), which exhibits a pretty low solubility value (Figure S1) thanks to its two bulky hydrophobic groups. Interestingly, galvanostatic cycling shows DTBHQ undergoes virtually no capacity loss after 500 cycles (over 350 h) as shown in Fig. 1. This exceeds by far state-of-the-art small molecules, despite the test cell contained 1.5 mL of electrolyte per mg of DTBHQ. This is in contrast to most reports claiming extended capacity retention of small quinone derivatives by using coin or Swagelok®-type cells that typically contain 300 μL of electrolyte per mg of active material [3] (Table S1). Under these conditions, we believe the extended capacity retention of DTBHQ is a significant result. As a matter of fact, the maximum solubility of DTBHQ was determined to be 629 μM/L and estimated to ≈ 100 μM/L in the oxidized quinone form (see Figure S1 and corresponding text for more details), which is at least 10 times below that of other small quinone derivatives used in AZIBs so far (Figure S1b and Table S1).

To investigate the electrochemical mechanism, we performed CV measurements of DTBQ/DTBHQ-based electrodes (Fig. 2a). CVs in black and red were both collected in K<sup>+</sup> electrolytes in acidic media (pH 0.40 and 4.87). Interestingly, a large difference of ca. 792 mV in the cathodic peaks was observed in these two electrolytes. Such potential shifts indicate that K<sup>+</sup> is certainly not participating as a major charge carrier in the reduction process. Alternatively, H<sup>+</sup> would be the main inserted cation. According to this scenario, the observed huge potential shift could be explained on the basis of the amphoteric behavior of water (two proton donors species) with its two pK<sub>a</sub> values: pK<sub>a</sub>(H<sub>3</sub>O<sup>+</sup>/H<sub>2</sub>O) = 0 and pK<sub>a</sub>(H<sub>2</sub>O/OH<sup>-</sup>) = 14. At this stage, let us recall that the equilibrium redox potential of DTBHQ/DTBQ-based electrode is first expressed by the general Eq. (1) at 25 °C with a slope of - 59.2 mV/pH [15],  $a_Q = a_{H_2Q} = 1$  for solids:

$$E_{eq} = E^\circ(Q/H_2Q) + \frac{0.0592}{2} \cdot \log \frac{a_Q \cdot (a_{H^+})^2}{a_{H_2Q}} = E^\circ(Q/H_2Q) - 0.0592 \cdot pH \quad (1)$$

At the local scale, as the reduction of the quinone form (Q) proceeds (a) an auxiliary protonation reaction occurs (b) giving rise to the hydroquinone form H<sub>2</sub>Q in presence of an appropriate proton source. The

involved proton source is necessary related to a Brønsted-Lowry acid (AH) present in the electrolyte; the latter being involved in another chemical equilibrium characterized by its corresponding K<sub>a</sub> (or pK<sub>a</sub>) value (c).



Combining those reactions allows us to express a potential dependence for the reduction process in terms of pK<sub>a</sub> by using the Henderson-Hasselbalch equation related to the involved acid/base couple (AH/A<sup>-</sup>):

$$\begin{aligned} E_{red} &= E^\circ(Q/H_2Q) - 0.0592 \cdot pH \\ &= E^\circ(Q/H_2Q) - 0.0592 \cdot pK_a - 0.0592 \cdot \log \frac{a_{A^-}}{a_{AH}} \end{aligned} \quad (2)$$

Therefore, considering two different electrolytes with their own proton donor, the relative shift in the reduction potential ( $\Delta E_{red}$ ) should be directly proportional to  $\Delta pK_a$  between the two different proton donors. It is also important to mention that local pH is governed by the dynamic equilibrium between acid (AH such as free H<sub>3</sub>O<sup>+</sup> or H<sub>2</sub>O proton donor) and base (A<sup>-</sup> such as H<sub>2</sub>O or *in-situ* electro-generated OH<sup>-</sup>). [13,14] The local pH at the composite electrode interface will be governed by the pK<sub>a</sub> value of the proton source according to the step c. The local buffering effect occurring approximately within pK<sub>a</sub> ± 1 of the considered AH/A<sup>-</sup> couple ( $\log(\frac{a_{H^+}}{a_{AH}}) \approx 0$ ) [13]) would therefore result in the stabilization of the reduction potential (*i.e.*, in a reduction peak). This in turn translates to a shift in the reduction potentials, which can be expressed as follows for two chosen proton sources characterized by pK<sub>a1</sub> and pK<sub>a2</sub>:

$$\Delta E_{red} = E_{red(2)} - E_{red(1)} = 0.0592 \cdot (pK_{a2} - pK_{a1}) = 0.0592 \cdot \Delta pK_a \quad (3)$$

In the more acidic electrolyte (pH 0.40), the concentration of free proton is high ([H<sub>3</sub>O<sup>+</sup>] ≈ 0.4 M) and it can trigger proton coupled reduction process (schematically shown in Fig. 2b) giving rise to a sharp reduction peak located at a potential of + 250 mV vs AgCl/Ag. As the electrolyte is extremely acidic, we anticipate that the reduction process occurs without a significant increase in the local pH at the electrode surface. In the KCl electrolyte (pH 4.87), the reduction peak is moved to - 542 mV vs AgCl/Ag. This experimental potential shift of 792 mV aligns quite well with the calculated one ( $\Delta E_{red} = 828.8$  mV, from Eq. (3)) based on the  $\Delta pK_a = 14.0$  considering the two proton donors: H<sub>3</sub>O<sup>+</sup> in HCl vs H<sub>2</sub>O in KCl. Therefore, it represents an increase of the local pH to 13.80 in KCl electrolyte. These results thus refute the intercalation of K<sup>+</sup> ions in DTBQ during reduction and corroborate that H<sup>+</sup> is the main

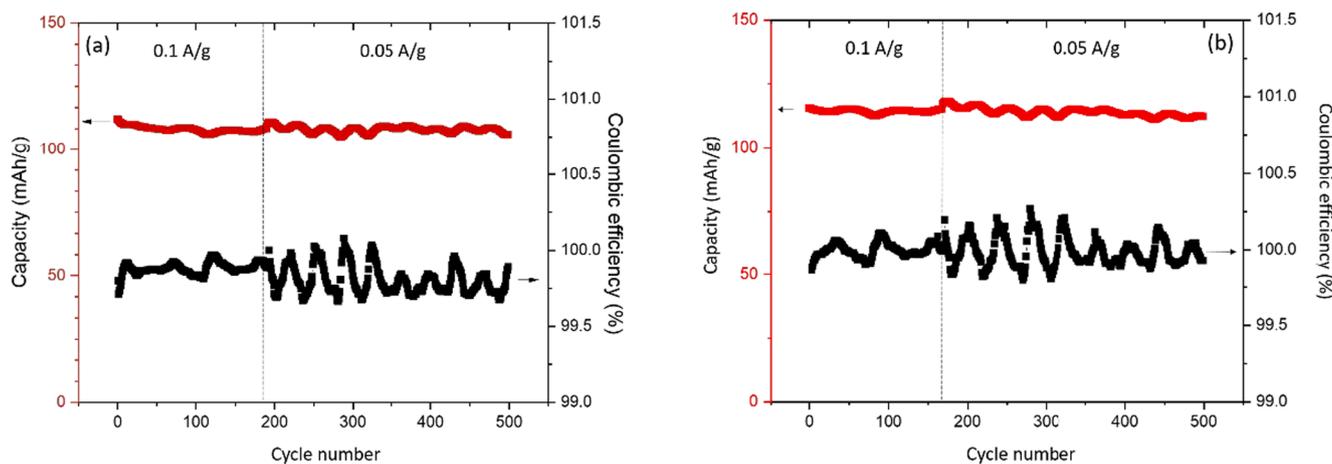
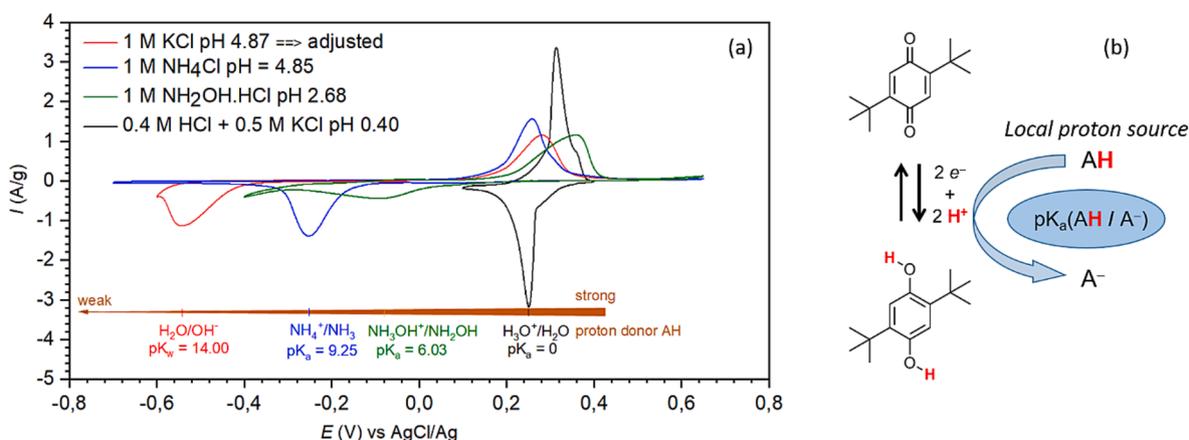


Fig. 1. Galvanostatic cycling of DTBHQ conducted at 0.1 and 0.05 A/g using 1.5 mL of 1.25 M Zn acetate electrolyte per milligram of DTBHQ with (a) a carbon counter electrode and (b) a zinc foil negative electrode. The capacitance of the carbon additive was subtracted. Fluctuations in capacity and efficiency correspond to changes in temperature between day and night.



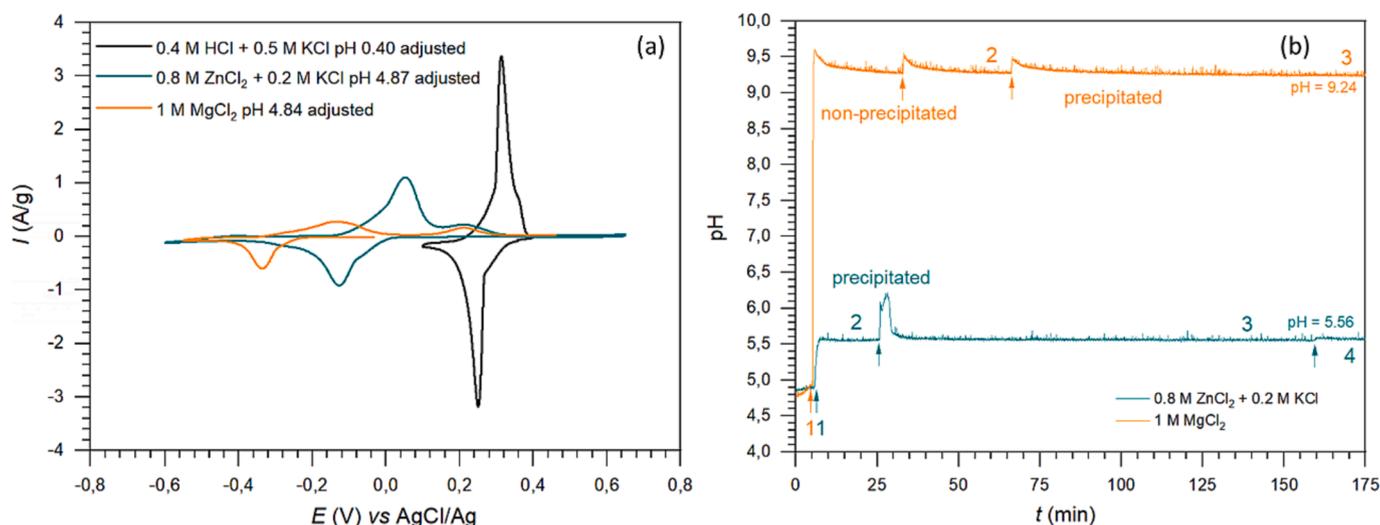
**Fig. 2.** (a) Representative CV traces of DTBQ/DTBHQ electrodes recorded in various aqueous electrolytes at 0.5 mV/s. The electrolyte composition and the initial bulk pH are mentioned in the legend. DTBQ/DTBHQ (50:50 wt%) were used as the working electrodes. (b) A schematic summarizing the crucial role of the involved proton donor in the overall reduction process of DTBQ in the solid state.

charge carrier. Moreover, the CV measurement in blue (Fig. 2a) was collected in 1 M NH<sub>4</sub>Cl (bulk pH 4.85; pK<sub>a</sub>(NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub>) = 9.25) at the same scan rate. The reduction potential (-254 mV) in this case is shifted by +288 mV as compared to KCl electrolyte despite the same initial bulk pH. This positive shift is in full agreement with the  $\Delta pK_a = 4.75$  (or  $\Delta E_{red} = 281.2$  mV from Eq. (3) considering the two proton donors in NH<sub>4</sub> and KCl electrolytes. Using an alternative proton donor from the ammonium family viz., NH<sub>3</sub>OH<sup>+</sup>/NH<sub>2</sub>OH but with a significantly lower pK<sub>a</sub> of 6.03 than that of NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub>, the CV reduction peak (Fig. 2a) is shifted further up by +166 mV, which aligns quite well with the value of  $\Delta E_{red} = 190.6$  mV expected from the  $\Delta pK_a = 3.22$  (Eq. (3)). The strong correlation between the measured  $E_{red}$  and the considered pK<sub>a</sub> value (Figure S2, Eq. (3)) therefore substantiates that H<sup>+</sup> recruited from AH proton donor should be the overwhelming cation paired with the faradaic capacity of DTBQ/DTBHQ.

It is noteworthy that oxidation peaks ( $E_{ox}$ ) in all these electrolytes are located within a narrow potential range between 257 and 362 mV vs Ag/AgCl whereas the onset of the reaction is quite similar for all of them. Therefore, considering kinetics effect (polarization) we believe peak potentials represent approximately the same level of acidification of the

local pH when H<sup>+</sup> are released back from DTBHQ.

Further insight was gained by using divalent cations (Zn<sup>2+</sup> and Mg<sup>2+</sup>) based electrolytes. CVs in cyan and orange were collected in ZnCl<sub>2</sub> and MgCl<sub>2</sub> electrolytes with an identical initial bulk pH  $4.85 \pm 0.02$  (Fig. 3a). Despite similar charge density of these two cations, the electrodes showed significantly different reduction potentials of -124 and -334 mV in ZnCl<sub>2</sub> and MgCl<sub>2</sub> electrolytes, respectively ( $\Delta E_{red} = 210$  mV). Considering the previous H<sup>+</sup> based mechanism  $\Delta E_{red}$  should however be approx. 130 mV based on Eq. (3) according to the pK<sub>a</sub> of the two weak Brønsted-Lowry acid/base couples [Zn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>/[Zn(H<sub>2</sub>O)<sub>5</sub>OH]<sup>+</sup> (pK<sub>a</sub> 9.0) and [Mg(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>/[Mg(H<sub>2</sub>O)<sub>5</sub>OH]<sup>+</sup> (pK<sub>a</sub> 11.2). [16] The observed  $\Delta E_{red} = 210$  mV therefore challenges the correlation with  $\Delta pK_a$ . However this misalignment can be explained by the *in-situ* buffering of the local pH that occurs well before reaching the pK<sub>a</sub> of AH due to precipitation of basic salts of Zn and Mg hydroxides and/or oxides [17–19]. This hypothesis was confirmed as pH of ZnCl<sub>2</sub> and MgCl<sub>2</sub> electrolytes were stabilized to 5.56 and 9.24 ( $\Delta pH = 3.68$ ) with concomitant formation Zn(OH)<sub>2(s)</sub>/ZnO and Mg(OH)<sub>2(s)</sub> precipitates (Figure S3 and S4) upon gradual additions of KOH Fig. 3(b). The  $\Delta pH = 3.68$  thus translates to  $\Delta E_{red} = 217.9$  mV, which is in fair agreement with



**Fig. 3.** (a) Representative CV traces of DTBQ/DTBHQ electrodes recorded in Zn<sup>2+</sup> and Mg<sup>2+</sup>-based aqueous electrolytes at 0.5 mV/s. The electrolyte composition and the initial bulk pH are mentioned in the legend. For comparison, the CV measured in 0.4 M HCl (Fig. 2a) was added. (b) pH monitoring of Zn<sup>2+</sup> and Mg<sup>2+</sup> based aqueous electrolytes (volume = 10 ± 0.5 mL) with the addition of 6 M KOH (20 ± 1 μL) at different times (indicated by arrows) until we noticed precipitation and stabilization of the pH. The corresponding images of the vial for the initial solutions (marked as no. 1) and precipitates (marked as no. 2, 3...) are also provided in Figure S3.

the observed  $\Delta E_{\text{red}} = 210$  mV in Zn and Mg electrolytes. In short, the proton mechanism is reiterated for divalent cations, although in this case, the shift in the reduction potential is primarily governed by  $\Delta\text{pH}$  at the interface rather than  $\Delta\text{p}K_{\text{a}}$  due to buffering effect (Figure S2). During the oxidation process, protons are released back from DTBHQ, which leads to the acidification of the local pH and re-dissolution of the hydroxide precipitates. [19] Due to the buffering effect however, the acidification of the local pH is mitigated until the precipitates are completely dissolved back into the solution [18,19] (low potential peak) and thereafter lead to a second peak the potential of which lies in the vicinity of those of monovalent cations (Fig. 2a).

#### 4. Conclusion

In conclusion, this study presents 2,5-Di-*tert*-butylhydroquinone as a promising active material for use in aqueous zinc-ion batteries. DTBHQ's maximum solubility was determined to be 629  $\mu\text{M/L}$ , significantly lower than that of other reported small quinone derivatives used in AZIBs, enabling remarkable capacity retention even at a high electrolyte to active mass ratio. The electrochemical activity of DTBHQ was explored in various aqueous electrolytes with mono- ( $\text{K}^+$ ,  $\text{NH}_4^+$  and  $\text{NH}_3\text{OH}^+$ ) and divalent ( $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$ ) cations, providing evidence that  $\text{H}^+$  is the primary inserted cation in the faradic process. According to this mechanism, free  $\text{H}_3\text{O}^+$  or  $\text{H}_2\text{O}$ , or  $\text{H}_2\text{O}$  molecules of cation solvation shell serve as a proton source, and therefore, the reduction process occurs in a potential range that scales with corresponding  $\text{p}K_{\text{a}}$  values. Further research and optimization of DTBHQ-based systems are warranted to fully exploit these findings.

#### CRediT authorship contribution statement

**Arvinder Singh:** Conceptualization, Data curation, Formal analysis, Writing – original draft. **David Grenz:** Data curation, Investigation. **Yann Pellegrin:** Data curation, Investigation. **Fabrice Odobel:** Data curation, Investigation. **Philippe Poizat:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Validation, Writing – original draft, Writing – review & editing. **Joël Gaubicher:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Validation, Writing – original draft, Writing – review & editing.

#### 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.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.elecom.2023.107559>.

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