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A mini review
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Mini Review

Zn electrode/electrolyte interfaces of Zn batteries: A mini review

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ABSTRACT

Zn metal batteries are promising for large-scale energy storage systems because of their extremely intrinsic safety and low cost. However, parasitic side reactions such as hydrogen evolution, Zn corrosion, and flourished dendrite growth behavior impede their practical implementation. Notably, electrode/electrolyte interface plays a critical role in regulating Zn deposition and improving the cyclic lifespan of rechargeable Zn metal batteries. Here, the fundamentals of Zn electrode/electrolyte interface and the related issues are discussed. Thereafter, competent strategies including artificial protective layers, electrolyte optimization, structural engineering to fulfill a stable working Zn metal anode are presented. Subsequently, progressive characterization techniques reveal interfacial chemistries and morphological evolution of Zn metal anodes are outlined. Finally, the significantly perspective to guide and promote the developed of Zn batteries are proposed. This review will serve to further advance the development of interfacial engineering for Zn metal anodes.

1. Introduction

Zinc (Zn) metal anode is promising for rechargeable batteries because of its high theoretical capacity (820 mAh·g−1, 5854 mAh·cm−3), low electrochemical potential (−0.762 V vs. SHE, standard hydrogel electrode) and intrinsic safety, which booms rechargeable Zn batteries prosperity[1–8]. However, Zn anode suffers from inherent restrictions for practical implementations including poor chemical stability and mean electrochemical reversibility[9–12]. It is well known that a dense Zn3(3OH−)6 passivation layer is formed on metallic Zn surface, when it is exposed to air[13]. This passivation layer is compact and homogeneous to prohibit further Zn corrosion in the air[14–15]. In a working battery, the charge/discharge process accompanies charge carriers (such as Zn2+, H+ in Zn batteries) migration and electrons transfer through contacted Zn anode/electrolyte interface. The interfacial reactions also occur between electrolytes and Zn electrodes surface, which trigger the formation of space-charge layer with mobile carriers redistribution near the interface, due to different chemical potential of solid Zn electrode and liquid electrolyte. The Zn2+ carries traverse the Zn electrode/electrolyte interface accords to the following steps: firstly, solvated ions Zn2+ ions migrate in liquid substance based on the diffusion mechanism; secondly, solvated Zn2+ ions are stripped from the solvent sheath of at the interface, which is the rate-determining step. Therefore, the Zn electrode/electrolyte interface shows a dominant effect on the growth mode of Zn.

Recently, tremendous achievements in designing Zn electrode/electrolyte interphase have been acquired to improve the electrochemical performance of Zn batteries. However, there is still a long way to fully solve the issues of metallic Zn electrode, especially in aqueous electrolyte and implement stable electrochemical cycling with a high Zn reversibility. In this minireview, we specialize on the fundamental scientific understanding of basic characteristics, challenges and strategies on the Zn electrode/electrolyte interface for stable Zn batteries, as well as the future perspectives in this field.

2. Zn electrode/electrolyte interfacial characteristics and issues

In alkaline electrolytes, the OH− can grievously corrode the Zn anode to form by-products of Zn(OH)2 and/or ZnO, which issue in ungratified compatibility with Zn anodes surface and dendrite flooding[16–18]. With regard to the alkaline electrolytes, the arisen mild aqueous electrolytes such as ZnSO4, Zn(CF3SO2)2 and Zn(TFSI)2 solutions significantly weaken the generation of the by-products, thus rendering much better compatibility with the Zn anode. Beyond that, compared with aqueous electrolytes, Zn metal shows higher thermodynamic stability in the organic solvents, which results in higher reversibility of Zn redox and thus enhances the Coulombic efficiencies of Zn plating/stripping. More importantly, organic electrolytes simplifies

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the electrochemistry at the Zn-anode surface by avoiding the unwanted passivation products, i.e., ZnO and Zn(OH)$_2$, which also provide favorable compatibility with Zn anode, but the low ionic conductivity and intrinsic toxicity issues limits their practical implementations.

Compared with liquid electrolytes, the (quasi-) solid-state electrolytes such hydrogel electrolytes, polymer electrolytes, ceramic electrolytes and hybrid electrolytes, are promising strategies to improve the compatibility of the electrolyte with Zn anode, due to little or no presence of free H$_2$O molecules trapped in their framework, remarkably suppressing side reaction. However, low ion conductivity and poor interface contact between electrode and electrolyte are great challenges for solid-state electrolyte.

Therefore, proper interface engineering becomes an easy and convenient solution to solve these issues. Current efforts in alleviating the interfacial compatibility mainly include modifying the electrodes, optimizing electrolytes and designing special architectures, which can prolong battery lifetimes.

2.1. Physical contact

The requirements of ions migration and electrons transfer in the interface of electrode and electrolyte necessitates the benign physical contact of electrode and electrolyte. The liquid electrolyte with excellent fluidity potentially shows superior compatibility with solid electrode. Similarly, due to good flexibility of gel electrolyte, gel electrolyte containing a certain amount of liquid electrolytes can undertake an effective contact with rigid electrode. However, in practical working batteries, there are several side reactions with by-products formed at the interface, such as Zn(OH)$_2$, Zn(OH)$_4$~2~, ZnO, Zn$_x$SO$_4$(OH)$_{2-x}$H$_2$O, Zn$_x$(CO$_3$)$_2$(OH)$_{6-x}$, which may retard Zn$^{2+}$ migration[16,19] (Fig. 1a).

For solid-state electrolyte, the physical contact of electrolyte and electrode is point-to-point contact and abundant micro voids exist at the interface among this point contact, where thus batteries have been plagued by a large interfacial impedance and sluggish solid–solid interface kinetics (Fig. 1b). The solid interfaces with favorable bifunctional conductivity for electron and ion are essential in principle, but the complex interfaces involve in physics, chemistry, and mechanics, lying at the heart of the solid-state battery concepts[20–21]. Meanwhile, the volume changes of the electrodes over a charge/discharge cycles with the formation and propagation of cracks, have prevented retention over many cycles of a solid–solid electrode–electrolyte interface[22–23]. These observations motivate to explore avenues for creating the interface interstitial layer for a rechargeable Zn anode with a solid-state electrolyte.

2.2. Electrochemical procedures at the Zn anode/electrolyte interface

The electrochemical procedures at electrode/electrolyte interface are critical factors for battery operation. The unstable interface will lead to the issues of Zn dendrite growth, by-product formation, hydrogen evolution, electrode passivation and dissolution, especially in aqueous electrolyte, which will cause poor cycling stability and safety issues (Fig. 2)[24–25]. On the other hand, the electrochemical reactions at interface are always affected by solvation/de-solvation process, diffusion kinetics and transport pathway, which is determined by the structure and composition of the interface and electrolyte[26]. Therefore, a fundamental look of electrochemical behavior and resulted products inspire us to ornament the interface.

In the Zn battery system, the Zn deposition process including nucleation at interface and Zn$^{2+}$ migration is driven by the concert electric field. There is an energy barrier between Zn$^{2+}$ and Zn metal for the formation of a new solid phase[27]. The solvated Zn$^{2+}$ situated in the electric double layer requires to overcome an energy barrier to desolvate and releases lots of electrochemical reactive water molecules [28]. After that, de-solvated Zn$^{2+}$ continuously deposits on the solid layer, which is determined by electric filed and ion concentration gradient of electrolyte[29]. The ions are apt to aggregate at the concentrated electric field (known as “tip” effect) and thus expedite Zn dendrite growth. The Zn nucleation and subsequent growth are pivotal to the stability of Zn deposition[29–30].

In addition, metallic Zn is thermodynamically unstable in widely used aqueous electrolyte[5,25,31–34], where Zn deposition even during shelf time is continuously interfered by competitive hydrogen evolution through H$_2$O decomposition (Zn + 2H$_2$O $\rightarrow$ Zn(OH)$_2$ + H$_2$) by consuming both the electrolyte and active Zn metal. The continuous hydrogen evolution will cause local pH changes, which further induces the formation of loose and brittle Zn$_x$SO$_4$(OH)$_{2-x}$H$_2$O (3Zn (OH)$_2$ + ZnSO$_4$⋅xH$_2$O $\rightarrow$ Zn$_x$SO$_4$(OH)$_{2-x}$H$_2$O by combining with the OH$^-$ and SO$_4^{2-}$ in the electrolyte [35–41]. It is generally assumed that these by-products augment the tortuosity and irregularity at the electrode/electrolyte interface with contact surface increased, which further accelerates the hydrogen evolution reaction. These issues necessitate an effective method to terminate this side reaction.

As a matter of fact, the issues of Zn dendrite growth and hydrogen evolution concurrently presents and interacts with each other. The hydrogen evolution reaction induces the non-uniform surface and electrode polarization at the electrode/electrolyte interface, which brings about concentrated electric field and thus the formation of Zn dendrite. The generation of Zn dendrite increases the surface of Zn anode, which can further accelerate the hydrogen evolution reaction. Therefore, several strategies have been designed to modify interfacial properties to regulate Zn deposition and suppress side reactions. In the following sections, we will discuss these design strategies for amelioration of Zn anode/electrolyte interface in detail.

3. Strategies to ameliorate Zn anode/electrolyte interface

The strategies such as surface modification (artificial solid electrolyte interface (SEI), physically coating, chemical decoration), electrolyte optimization (additives, gel, organic, solid electrolyte), structural design (alloying, 3D current collector), etc. have been widely applied in the Zn anode/electrolyte interface. The mechanisms and effects of these strategies are mainly discussed in this part.
3.1. Artificial protective layers

The construction of protective layers between Zn electrode and electrolyte is considered to be one of means to regulate Zn deposition and suppress side reaction of hydrogen evolution via water decomposition. Both ex-situ physical coating and in-situ chemical pretreatment methods are employed to construct interfacial layers. These interfacial layers partly avoid chemical and electrochemical reaction of Zn electrode with electrolyte through isolating electrode and electrolyte. Meanwhile, the interfacial layers with sufficient mechanical strength stick up to volume change and dendrite growth.

Up to now, several physical coverages with neither electronic nor...
ionic conductivities such as TiO$_2$, CaCO$_3$, ZrO$_2$, Ti$_3$C$_2$Tx, MXene and MoS$_2$ inorganic materials are utilized as insulating layers at Zn electrode/electrolyte interface to directly block Zn dendrites[42–45]. These insulating layers don’t participate in any chemical and electrochemical reactions. They allow electrolyte to permeate into this layer and form a super-concentrated electrolyte front Zn electrode surface, which will result in a homogeneous Zn deposition and further alleviate dendrites [46–49]. The coating layer with high porosity rejects the large fraction of water via partial de-solvation in advance. The Zn deposition occurs near the reaction interface underneath coating layer owing to its electric insulation properties. So, metallic Zn affinity is a pivotal criterion to estimate the feasibility of coating materials. Among above-mentioned inorganic materials, the TiO$_2$ shows contrastingly different metal affinity with different facets of TiO$_2$ exposed to Zn electrode surface. When using C-TiO$_2$ with (1 0 0) facet exposed as the coating layer, Zn tends to grow on the surface of TiO$_2$ layer with a higher Zn affinity. Whereas, the coating F-TiO$_2$ with highly exposed (0 0 1) facet on commercial Zn foil shows low metal affinity and is utilized protective layer to guide Zn$_{2+}$ uniform nucleation and further deposition (Fig. 3a). The as-prepared ZF@F-TiO$_2$ electrode can be cycled steadily over 460 in symmetric cells[50].

In addition to above-mentioned inorganic coating, polymer material coating is also a good choice to solve deep-seated issues of dendrite growth and intricate side-reactions. Among them, the polyamide can strongly coordinate with Zn$_{2+}$, establishing a diffusion layer on Zn electrode[51]. The resulted polyamide interface increases the electrochemical polarization and the nucleation overpotential of Zn deposition. In return, the number of active sites for nucleation significantly increases and the grain size of the Zn deposit is eventually refined[52–55]. The built solid interface also serves as a buffer layer to isolate active Zn electrode from bulk aqueous electrolytes, thus suppressing free water/ O$_2$-induced corrosion and passivation (Fig. 3b). The polymer-modified Zn electrode exhibits a 60-fold enhancement in running lifetime compared to the bare Zn electrode.

The above discussed SEIs are fabricated by simply blade coating method. The coating layers are inhomogeneous and uncompacted, which are hard to availably isolate electrolyte from the Zn electrode surface. The side reactions of Zn corrosion and hydrogen evolution reactions still occur on the uncovered Zn surface. On the other hand, such coating layers feature poor adhesion and are easily detached from the Zn electrode results from volume changes during cycling. In addition, these coating layers are not Zn$_{2+}$ ion conductors due to higher electric charge density of Zn$_{2+}$ and high energy barrier of Zn$_{2+}$ transfer. Hence, an in-situ construction method is required for a dense and homogeneous SEI with strong adhesion and a high Zn$_{2+}$ transfer number. The Zn electrode with three-dimensional nanoporous ZnO architecture modified (denoted as Zn@ZnO-3D) is designed by in-situ Zn(OH)$_2^-$ deposition[51]. The Zn@ZnO-3D not only avoids the “tip effect” via uniform 3D distribution but also improves the kinetics through reducing the deposition barrier (only 42.4 mV nucleation overpotential at 1 mA cm$^{-2}$) (Fig. 3c). As a result, it prohibits the side-reactions during Zn deposition and improves reversibility of Zn plating/stripping. Similarly, a robust, dense and homogeneous ZnS interphase is in-situ constructed via a vapor–solid method at 350 °C[56]. The bonding interaction of S atoms in the ZnS and Zn atoms in the Zn metal induces an unbalanced charge distribution at the interphase (Fig. 3d, e). The unbalanced charge distribution enhances the Zn$_{2+}$ diffusion at the ZnS@Zn interphase as well as the adhesion of the ZnS layer to the Zn metal. Accordingly, the ZnS film contributes to improve the reversibility of Zn metal and avoid the electrolyte-induced side reactions in mild electrolyte. The ZnS@Zn/ZnS@Zn symmetrical cell exhibits longer lifespan of >1100 h at 2 mA h cm$^{-2}$ and the MnO$_2$/ZnS@Zn full cell shows excellent cycling stability with 87.6% capacity retained after 2500 cycles.

### 3.2. Electrolyte optimization

During cyclic charge/discharge processes, the interface status is related to electrolyte components including solvents, salts, and additives. The dendrite deposition during metal deposition can be hindered by adding other positive ions with lower reduction potential in the electrolyte according to electrostatic shield theory[57]. The Na$^+$ shows a lower reduction potential than that of Zn$_{2+}$ and a thin layer of Na$^+$ protection shell. So, the ZnSO$_4$ solution with the existence of Na$_2$SO$_4$ could effectively suppress the growth of Zn dendrites (Fig. 4a)[58–60]. On the other hand, the concentration of electrolyte also displays a decisive influence on electrolyte properties and interfacial stability. In addition, highly concentrated electrolytes show the unique solvation-shearth structure of Zn$_{2+}$, where the high population of anions gathers in the vicinity of Zn$_{2+}$ to constitute close ion pairs of (Zn-TFSI)$^-$ . The extensive existence of (Zn-TFSI)$^-$ can effectively suppress the presence of (Zn$_2$(H$_2$O)$_2$)Zn$^{2+}$ in aqueous electrolytes and the defluorination reaction of LiTFSI occurs at a potential above that of H$_2$ evolution, favoring for the formation of SEI, which provide an unheard-of opportunity to resolve the irreversibility and side reaction issues of Zn electrode (Fig. 4b)[5]. Meanwhile, highly concentrated electrolyte could rapidly augment ion content on the Zn anode surface and promote uniform Zn deposition. Nevertheless, the underlying mechanism of SEI formation is not entirely studied.

A new Zn(TFSI)$_2$/acetamide eutectic electrolyte is designed for in-situ formation of a Zn$_2$-rich organic/inorganic hybrid SEI via cation solvation modulation. The formation of Zn–O coordination and intermolecular interactions contribute the formation of eutectic solutions (Fig. 4c). In this electrolyte system, the ionic interplay strength can be tuned via changing ratio of the Zn(TFSI)$_2$/acetamide (Fig. 4d, e). The [Zn(TFSI)(Ac)$_2$]$^+$ exhibits the most uniform molecular electrostatic potential energy surface distribution along with relatively low total binding energy, making the anion derived SEI formation for metallic Zn. The SEI can is highly permeable for Zn ions (0.572 for Zn$^{2+}$ transfer number) and prevents excess Zn consumption by blocking solvents and electrons [61–63]. As a result, dendrite-free and intrinsically stable Zn plating/stripping can be realized at the areal capacity of >2.5 mAh cm$^{-2}$ or even under a common dilute aqueous electrolyte system. The solvation structure of the cations can also be modulated by using organic electrolyte[64–66]. The primary solvation shell of Zn$^{2+}$ occupied by succinonitrile molecules can reduce the affinities between Zn$^{2+}$ and water, thus alleviating side reactions at the Zn electrode/electrolyte interface (Fig. 4f)[31]. This is attributed to the increase of the Zn$^{2+}$ de-solvation energy in a moderate way.

Polymer electrolyte features lower fluidity and the inevitable electrostatic interaction between the positively charged electrolytic ions and functional groups, leading to the formation of a (quasi-) SEI layer. The charged sulfonate groups on the side chains of zwitterionic sulfobetaine hydrogel can induce the formation of quasi-SEI layer, thus inducing the uniform and homogeneous deposition of Zn$_{2+}$ ions onto the anode (Fig. 4g)[67]. The SEI consisting of ZnF$_2$, zinc borate and ZnS is also observed in the poly(1,3-dioxolane) electrolyte. The contents of ZnF$_2$, ZnS and zinc borate are beneficial for uniform Zn$_{2+}$ deposition and inhibits the formation of Zn dendrite during cycling[68].

### 3.3. Structural design

The structural engineer of Zn electrodes through constructing 3D configurations/hosts offers an available opportunity to homogenize the electric field distribution[69–70]. Meanwhile, the 3D structure of electrode affords a lower nucleation overpotential, fast electron transport and sufficient electrolyte contact. For example, the electric field streamlines are more uniform in 3D CC@CNT scaffold than that of bare CC. The homogeneously distributed electric field effectively escapes the “tip effect”, which assures evenly plated Zn onto the CNT surface at the early stage and further extension of cycling duration (Fig. 5a)[71–72].
Similarly, 3D metal–organic framework (MOF) of ZIF-8 with large cages interconnected via small six-membered ring apertures is utilized as a host material for 100% high-efficiency and dendrite-free Zn plating/stripping (Fig. 5b) [39]. Besides the utilization of 3D Zn electrode, alloying of Zn metal with metals offers an alternative strategy. A eutectic-composition Zn$_{88}$Al$_{12}$ alloy with a lamellar structure is designed based on Zn/Al alloy system, where the Al$_2$O$_3$ shell on the Al lamellas prohibits the dissolution of Al and thus affords the selective Zn deposition. On the other hand, the insulating Al$_2$O$_3$ shell blocks the electron transfer from Al to the Zn$_{2+}$ and the positively electrostatic shield formed around the Al/Al$_2$O$_3$ lamellas guide the uniform Zn deposition (Fig. 5c) [73].

Most studies focus on the design of Zn anodes, the prosperity of Zn batteries prompt us to analyze other components including separators. Separator is a pivotal component in battery to avoid physical contact of the cathode and the anode, and it can be viewed as an extension of the electrode. So, the structural engineering of separator offers an opportunity to ameliorate Zn growth. A Janus separator is designed by directly growing vertical graphene carpet on commercial glass fiber separator. The Zn@3D vertical graphene viewed as the 3D continuation of Zn anode can effectively homogenize electric field distribution and lower the local current density (Fig. 5d) [74–76].

4. Characterization on interface of Zn anode/electrolyte

To solve problems regarding Zn anodes, in-depth understanding of the interfacial chemistries, Zn deposition behaviors and their interrelationships are of significance for guiding the rational design of the Zn anode/electrolyte interface. Therefore, the precise characterization and analysis on Zn metal anodes are crucial. Many electrochemical methods, in-situ observations, ex-situ methods and theoretical analysis have been developed to investigate the feature of the interface (Fig. 6). This section will discuss state-of-the-art characterization techniques for studying Zn metal anodes.

Recently, in-situ optical observation for the deposition and dissolution of Zn anode and parasitic side reaction at micrometer scale is conducted utilizing a well-designed transparent chamber. However, the widely used application of this characterization is limited due to its low resolution. Generally, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) is regarded as the most widely applied tool for visualizing the surface morphology of electrochemical Zn deposition metal anodes under high resolution. To avoid the impact of air and moisture on electrode, in-situ SEM and TEM are regarded to be promising for visualizing electrochemical Zn deposition [77–79].

Moreover, X-ray photoelectron spectroscopy (XPS), X-ray diffraction
(XRD), Raman and Fourier-transform infrared spectroscopy (FTIR) are valid to identify the components and chemical bonds of the SEI film. Other advanced characterization method, such as neutron scattering, synchrotron X-radiation (SXR) also has related applications. However, post-mortem studies on the SEI could be disturbed by operational or environmental factors, which may not fully reflect what is truly taking place. Therefore, the development of in-situ spectroscopy measurements is critical in unveiling the surface chemistry of actual Zn anodes.

Although several advanced techniques are utilized to study interfacial chemistries of Zn anode, the present understanding of the interfacial behavior is still limited, due to their complicated components and dynamical process. Theoretical analysis such as density functional theory (DFT) calculation, molecule dynamic (MD) simulation and COMSOL Multiphysics as an auxiliary means of experiments needs to be applied and developed, especially under realistic operation conditions and dynamic process simulation. Among them, the charge density distributions and the absorption energy calculated by DFT are the most popular theoretical analysis methods, which helps to elucidate electrochemical reactions on the interface more deeply. The MD simulation can imitate the solvation structure of the Zn\(^{2+}\) in the electrolyte, which is conducive to reasonably deduce the interaction between the electrolyte and electrode. While, the COMSOL Multiphysics are employed to simulate the local current density and electric field at the surface of Zn electrode, which can explain the initial formation point of Zn deposition and further extension during cycling.

5. Conclusions and perspectives

Zn anode is thermodynamically unstable in aqueous environment accompanying side-reactions of hydrogen evolution and corrosion, and dendrite growth. The interfaces between Zn metal anode and electrolyte are basic route for Zn\(^{2+}\) ion transport in operational batteries. The interfacial properties are correlative to the formed compounds on the surface of the electrode, remarkably suppressing the ionic conductivity and mechanical strength. The interfacial engineering on Zn metal anode is promising for optimized ion diffusion and distribution, thus fulfilling a dendrite-free morphology as well as lowered side reactions, of life-or-death for the long-term stability of Zn metal batteries.

Extensive efforts have been paid on the interfacial engineering between Zn and liquid/solid electrolytes. Characterization techniques including SEM, TEM, XPS, AFM, FT-IR, Raman, et al. and theoretical simulations analysis, provide complementary and in-depth understanding of Zn metal interfaces, which boost fundamental look at the relationship of interfacial properties and the Zn deposition behaviors, and meanwhile guide the rational design of stable interface on the operational Zn metal anode.

A perfect interface possesses high electronic insulation but excellent ionic conductivity. Meanwhile, good mechanic strength and electrochemical stability are also required. To fulfill these criterions, electrolyte formulation, electrode modification and structural designs have been carried out. All these tactics exhibits effectiveness in formation a stable electrode/electrolyte interface on Zn metal anode by regulating the distribution of ions and electrons at the interface.

Despite the fruitful interface acquisitions yielded by researchers, there are still many challenges required to overcome for establishing efficient Zn metal interfaces.
1. The underlying complex interaction tenets of the artificial protective layer and Zn metal anode are yet to be in-depth seized to better reorganize the dynamic process from original solvated Zn-ion to final deposited Zn atom, which needs the closely collaboration of experiment, simulation, and theoretical calculations.

2. The compositional and structural optimization of the artificial protective layers, especially the hybridization of organic and inorganic components, with the assistance of various preparation methods to warrant a robust Zn metal protection especially under high current density or high capacity test conditions.

3. The unknown interfacial phenomena need to be unfolded by advanced characterization techniques to synthetical comprehending Zn anode/electrolyte interfaces. In-situ characterization techniques are highly desired to pursue the real-time interface evolution.

4. The fundamental look at the interfacial Zn deposition mechanism and dynamic growth behaviors at the interface and formed products under several working conditions, including different temperatures, pressure and electrolyte systems.

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.

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