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# On the interfacial phenomena at the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)/Li interface

Kostiantyn V. Kravchyk, Huanyu Zhang &amp; Maksym V. Kovalenko

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Research on the  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO)/Li interface is essential for improving the performance of LLZO-based solid-state batteries. In this comment, the authors present an analysis of the key interfacial phenomena at the LLZO/Li interface, highlighting recent developments and unresolved issues.

Diverse methods for cleaning the  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) surface and utilization of an interfacial layer (IL) between garnet-type LLZO solid-state electrolyte and lithium metal anode are widely recognized as critical strategies to enhance the electrochemical performance of Li-garnet solid-state batteries<sup>1–3</sup>. Despite the growing interest in developing efficient cleaning methodologies and efficient ILs for the Li/LLZO interface, a literature review reveals a lack of consensus within the research community regarding their actual function. While it is generally agreed that both approaches often improve lithium wettability on the LLZO surface, thereby reducing interfacial resistance and voltage polarization, significant debates persist regarding the specific mechanisms occurring during Li plating and stripping at cleaned/IL-functionalized LLZO surfaces during cycling. Furthermore, understanding how the interface evolves during Li plating and stripping cycles remains challenging, primarily due to the complexity of examining the Li/LLZO interface compared to characterizing the Li surface in liquid Li-ion batteries.

Given the importance of unveiling the impact of LLZO surface cleaning and the application of ILs, this commentary summarizes their primary functions by considering experimentally and computationally validated phenomena occurring during Li plating and stripping at the Li/LLZO interface. Numerous review and perspective articles addressing ILs for the Li/LLZO interface<sup>4–10</sup> present a broad overview of various ILs and their reported electrochemical performance, but still lack to offer a broader comprehension of the fundamental processes occurring during Li plating and stripping. This commentary seeks to address this gap by providing a concise analysis of the key interfacial phenomena at the Li/LLZO interface.

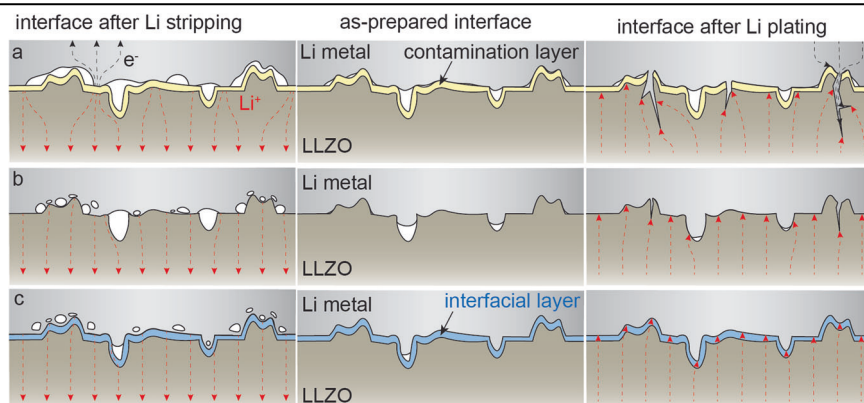
## Analysis

Let us begin our analysis by discussing the configuration of the LLZO/Li interface without specific LLZO surface cleaning or adding an artificial IL, followed by examining the processes occurring during Li plating and stripping (Fig. 1a). It is important to note that the LLZO surface rarely remains pure during storage and handling<sup>11</sup>. As revealed by numerous X-ray photoelectron spectroscopy measurements<sup>12–15</sup>, LLZO reacts with  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , forming a contamination layer primarily composed of  $\text{Li}_2\text{CO}_3$  and  $\text{LiOH}$ . This issue not only increases the interfacial resistance of the Li/LLZO interface, thereby causing voltage polarization but also significantly enhances the lithiophobicity of the LLZO surface. Lithiophobicity of LLZO has been experimentally demonstrated in multiple studies examining the

contact angle of molten Li on the LLZO surface<sup>16–18</sup>. The implications of a lithiophobic contaminated LLZO surface extend beyond just the challenge of establishing full contact with the Li metal anode. Considering reports on liquid-state Li metal batteries suggesting that the lithiophobicity/lipophilicity of current collectors can alter the morphology of deposited Li<sup>19–21</sup>, similar behavior, although not yet confirmed, can also be foreseen in solid-state systems. This correlation can be explained by the fact that dendritic Li tends to form on lithiophobic surfaces as plated Li seeks to minimize contact with the surface. Conversely, Li plating on a lithiophilic surface tends to maximize contact, promoting more uniform, non-dendritic structures. Moreover, the lithiophobicity of the contaminated LLZO surface plays a detrimental role during Li stripping, particularly in promoting the formation of voids at the Li/LLZO interface – a common problem during Li stripping when the rate of Li removal exceeds the rate of Li diffusion within the metal<sup>1,22</sup>. This occurs because Li tends to minimize contact with the lithiophobic LLZO surface, which amplifies void formation. The formation of voids can significantly decrease cycling stability, leading to increased current densities during subsequent plating, which may ultimately result in dendrite formation.

To address the issues associated with contaminated LLZO surfaces, Sun et al.<sup>23</sup>, Kravchyk et al.<sup>13</sup> and others<sup>12,15,24</sup> demonstrated that cleaning the LLZO surface can significantly reduce Li/LLZO interfacial resistance while also playing a crucial role in mitigating the formation of Li dendrites and voids (Fig. 1b). Contact angle measurements performed by Sakamoto et al.<sup>16</sup> revealed that a contaminant-free LLZO surface is lithiophilic, with a contact angle of ca. 95° with molten metallic Li. These experimental observations align with computational results conducted by Liu et al.<sup>25</sup>, which showed negative surface energy values for the Li/LLZO interface compared to the more positive values computed for the Li/ $\text{Li}_2\text{CO}_3$  interface. This suggests that during Li plating on a lithiophilic LLZO surface, the plated Li tends to maximize contact with the surface, promoting more uniform and less dendritic structures. Additionally, during Li stripping, the lithiophilicity of the clean LLZO surface plays a favorable role by mitigating void formation at the Li/LLZO interface. This can be explained by the tendency of Li to maintain maximum contact with the lithiophilic surface, which helps reduce void formation by driving them into the Li metal rather than allowing them to persist at the Li/LLZO interface. Moreover, it should be noted that, in addition to cleaning the LLZO surface, various lithiophilic materials have been tested as interfacial layers between the LLZO surface and Li metal. A comprehensive list of studied interfacial layers can be found in the following reviews<sup>5,7,26</sup>. Notably, the deposition of interfacial layers at the Li/LLZO interface is performed only after the LLZO surface has been thoroughly cleaned, typically using methods such as thermal treatment<sup>13,14,25,27</sup>, wet chemical processes<sup>16,23,28–31</sup>, or polishing<sup>15,27,32</sup>. The application of ILs can further enhance lithium wettability on the LLZO surface, thereby reducing interfacial resistance and voltage polarization<sup>17,18,33–35</sup>. For instance, as demonstrated by Hu et al.<sup>18</sup>, the use of Al as IL resulted in a decrease in interfacial resistance

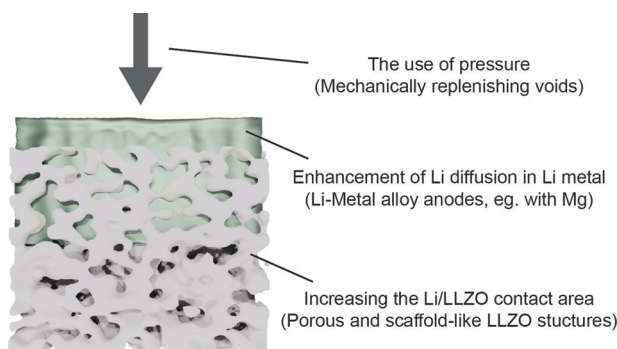
**Fig. 1 | Schematics of stripping and plating of Li at the Li/LLZO interface.** Drawing of the Li/LLZO interface based on a contaminated (a), cleaned (b), and the IL-functionalized (c) LLZO surface for as-prepared interface and after plating and stripping of Li. The figure illustrates key factors affecting Li-ion transport at the Li/LLZO interface, including the presence of voids and cavities (due to insufficient pressing of Li onto the rough LLZO surface), the  $\text{Li}_2\text{CO}_3/\text{LiOH}$  contamination layer (shown in yellow), and the interfacial layer (shown in blue) between metallic Li and LLZO.



from 950  $\text{Ohm}\cdot\text{cm}^2$  measured for pristine LLZO/Li interface to 75  $\text{Ohm}\cdot\text{cm}^2$ . The high lithiophilicity of this IL was also confirmed by complementary contact angle measurements with molten Li<sup>18</sup>, which revealed significant decrease of Li/LLZO contact angle to 47° compared to 95° observed for a merely cleaned LLZO surface<sup>16</sup>. These findings suggest that using such ILs could further improve the mitigation of void and Li dendrite formation, similar to the effects observed with clean LLZO surfaces (Fig. 1c). Lastly, it should be noted that both cleaning the LLZO surface and the employment of ILs might significantly improve the surface roughness of the LLZO surface. This factor can be as critical as lithiophilicity since, according to Ceder et al.<sup>36</sup>, the Li plating at an rough LLZO surface leads to a higher lithium deposition rate in the tip-like regions, causing the formation of the dendrites.

## Outlook

In summarizing our analysis of the effectiveness of LLZO surface cleaning and the application of various ILs, it is important to acknowledge that the intrinsic problem of void formation during Li stripping may still persist. This issue is particularly challenging at high current densities and areal capacities, such as those exceeding 1  $\text{mA cm}^{-2}$  and 1  $\text{mAh cm}^{-2}$ , where alternative strategies may be required to address void formation effectively. Below, we outline three potential strategies for mitigating this issue (see Fig. 2 for details):



**Fig. 2 | Schematic representation of additional strategies to mitigate void formation at the Li/LLZO interface.** Illustration of the Li/LLZO interface with a Li-metal alloy anode, LLZO scaffold, and applied external pressure, highlighting various void-mitigation strategies, including (i) the use of pressure, (ii) enhanced Li diffusion within the anode, and (iii) increased Li/LLZO contact area.

- The use of pressure: The formation of voids can be mitigated by applying pressure at the Li/LLZO interface, which helps mechanically replenish the voids. Studies by Sakamoto<sup>37</sup>, Janek<sup>38</sup>, Chen<sup>39</sup>, Srinivasan<sup>40</sup> and Kovalenko<sup>41</sup> have demonstrated that maintaining a critical stack pressure at a given current density can prevent void formation. However, higher current densities necessitate higher pressures, which could potentially induce cracks in the LLZO, leading to dendrite formation due to structural failures. Additionally, the use of bulky, heavy constructions to apply such pressures presents engineering challenges that could significantly reduce the volumetric and gravimetric energy densities of LLZO solid-state batteries.

- Enhancement of Li diffusion in Li metal<sup>38,42–45</sup>: While ILs play a crucial role, they are insufficient on their own to fully resolve void formation issues. Modifying the diffusion properties of Li metal is also essential. For instance, research by Janek et al.<sup>45</sup> has shown that introducing 10 at% Mg into the lithium metal anode significantly enhances Li diffusion compared to bare Li metal. However, experimental validation of improved cycling stability at the Li-Mg alloy/LLZO interface due to void mitigation is still pending.

- Increasing the Li/LLZO contact area<sup>46–54</sup>: This can be achieved by fabricating porous, scaffold-like LLZO structures, which allow Li to be plated and stripped within the pores, thereby increasing the Li/LLZO contact area and significantly reducing the local stripping current density. Computational studies performed by Kravchyk et al.<sup>55</sup> have shown that using 50% porous LLZO membranes with 5  $\mu\text{m}$  pore sizes can reduce the stripping current density by ca. 90%, effectively mitigating void formation at the Li/LLZO interface.

In conclusion, despite significant advancements in this field, the optimal LLZO/Li interface engineering remains a complex challenge. The most effective solution will likely involve a combination of approaches, including the employment of ILs, additives in Li metal, and the use of a porous LLZO surface. It is anticipated that within the next few years, these combined strategies will lead to superior cycling stability of Li metal with LLZO solid-state electrolytes at commercially relevant current densities and areal capacities.

Kostiantyn V. Kravchyk<sup>1,2</sup>✉, Huanyu Zhang<sup>1,2</sup> & Maksym V. Kovalenko<sup>1,2</sup>✉

<sup>1</sup>Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, 8093 Zürich, Switzerland. <sup>2</sup>Laboratory for Thin Films and Photovoltaics, Empa - Swiss Federal Laboratories for Materials Science & Technology, 8600 Dübendorf, Switzerland.

✉ e-mail: [Kostiantyn.Kravchyk@empa.ch](mailto:Kostiantyn.Kravchyk@empa.ch); [mvkovalenko@ethz.ch](mailto:mvkovalenko@ethz.ch)

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## References

- Krauskopf, T., Richter, F. H., Zeier, W. G. & Janek, J. Physicochemical concepts of the lithium metal anode in solid-state batteries. *Chem. Rev.* **120**, 7745–7794 (2020).
- Xu, L. et al. Garnet solid electrolyte for advanced all-solid-state Li batteries. *Adv. Energy Mater.* **11**, 2000648 (2021).
- Feng, W., Zhao, Y. & Xia, Y. Solid interfaces for the garnet electrolytes. *Adv. Mater.* **36**, 2306111 (2024).
- Jia, L. et al. Li–solid electrolyte interfaces/interphases in all-solid-state Li batteries. *Electrochem. Energy Rev.* **7**, 12 (2024).
- Duan, H. et al. Li/Garnet interface optimization: an overview. *ACS Appl. Mater. Interfaces* **12**, 52271–52284 (2020).
- Biao, J. et al. Perspectives on Li dendrite penetration in  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ -based solid-state electrolytes and batteries: materials, interfaces, and charge transfer. *Adv. Energy Mater.* **14**, 2303128 (2024).
- Wang, C. et al. Garnet-type solid-state electrolytes: materials, interfaces, and batteries. *Chem. Rev.* **120**, 4257–4300 (2020).
- Zhao, J. et al. Current challenges and perspectives of garnet-based solid-state electrolytes. *J. Energy Storage* **68**, 107693 (2023).
- Ji, W. et al. A review of challenges and issues concerning interfaces for garnet-type all-solid-state batteries. *J. Alloys Compd.* **979**, 173530 (2024).
- Zhang, L. et al. Recent advances of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ -based solid-state lithium batteries towards high energy density. *Energy Storage Mater.* **49**, 299–338 (2022).
- Huo, H. et al.  $\text{Li}_2\text{CO}_3$ : A critical issue for developing solid garnet batteries. *ACS Energy Lett.* **5**, 252–262 (2020).
- Sharafi, A. et al. Impact of air exposure and surface chemistry on Li– $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  interfacial resistance. *J. Mater. Chem. A* **5**, 13475–13487 (2017).
- Zhang, H. et al. On high-temperature thermal cleaning of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  solid-state electrolytes. *ACS Appl. Energy Mater.* **6**, 6972–6980 (2023).
- Wu, J.-F. et al. In situ formed shields enabling  $\text{Li}_2\text{CO}_3$ -free solid electrolytes: a new route to uncover the intrinsic lithiophilicity of garnet electrolytes for dendrite-free Li-metal batteries. *ACS Appl. Mater. Interfaces* **11**, 898–905 (2019).
- Cheng, L. et al. Garnet electrolyte surface degradation and recovery. *ACS Appl. Energy Mater.* **1**, 7244–7252 (2018).
- Sharafi, A. et al. Surface chemistry mechanism of ultra-low interfacial resistance in the solid-state electrolyte  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ . *Chem. Mater.* **29**, 7961–7968 (2017).
- Du, M. et al. Smart construction of an intimate lithium | garnet interface for all-solid-state batteries by tuning the tension of molten lithium. *Adv. Funct. Mater.* **31**, 2101556 (2021).
- Dubey, R. et al. Building a better Li-garnet solid electrolyte/metallic Li interface with antimony. *Adv. Energy Mater.* **11**, 2102086 (2021).
- Yan, K. et al. Selective deposition and stable encapsulation of lithium through heterogeneous seeded growth. *Nat. Energy* **1**, 16010 (2016).
- Sanchez, A. J. & Dasgupta, N. P. Lithium metal anodes: advancing our mechanistic understanding of cycling phenomena in liquid and solid electrolytes. *J. Am. Chem. Soc.* **146**, 4282–4300 (2024).
- Wood, K. N., Noked, M. & Dasgupta, N. P. Lithium metal anodes: toward an improved understanding of coupled morphological, electrochemical, and mechanical behavior. *ACS Energy Lett.* **2**, 664–672 (2017).
- Lu, Y. et al. The void formation behaviors in working solid-state Li metal batteries. *Sci. Adv.* **8**, eadd0510 (2022).
- Huo, H. et al. In-situ formed  $\text{Li}_2\text{CO}_3$ -free garnet/Li interface by rapid acid treatment for dendrite-free solid-state batteries. *Nano Energy* **61**, 119–125 (2019).
- Rajendran, S. et al. An all-solid-state battery with a tailored electrode–electrolyte interface using surface chemistry and interlayer-based approaches. *Chem. Mater.* **33**, 3401–3412 (2021).
- Zheng, H. et al. Intrinsic lithiophilicity of Li–garnet electrolytes enabling high-rate lithium cycling. *Adv. Funct. Mater.* **30**, 1906189 (2020).
- Yang, L. et al. Interrelated interfacial issues between a  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ -based garnet electrolyte and Li anode in the solid-state lithium battery: a review. *J. Mater. Chem. A* **9**, 5952–5979 (2021).
- Cheng, L. et al. The origin of high electrolyte–electrode interfacial resistances in lithium cells containing garnet type solid electrolytes. *Phys. Chem. Chem. Phys.* **16**, 18294–18300 (2014).
- Liu, X. & Huang, Z. Rapid treatment of LLZO solid electrolyte surface impurities by lactic acid solution. *J. Phys. Conf. Ser.* **2840**, 012018 (2024).
- Besli, M. M. et al. Effect of liquid electrolyte soaking on the interfacial resistance of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  for all-solid-state lithium batteries. *ACS Appl. Mater. Interfaces* **12**, 20605–20612 (2020).
- Ruan, Y. et al. Acid induced conversion towards a robust and lithiophilic interface for  $\text{Li}-\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  solid-state batteries. *J. Mater. Chem. A* **7**, 14565–14574 (2019).
- Shin, S., Lee, J., Shin, T. H. & Lee, S. Revealing the influence of in-situ formed LiCl on garnet/Li interface for dendrite-free solid-state batteries. *J. Energy Chem.* **92**, 394–403 (2024).
- Ma, X. & Xu, Y. Effects of polishing treatments on the interface between garnet solid electrolyte and lithium metal. *Electrochimica Acta* **441**, 141789 (2023).
- Chu, J. et al. Optimization strategies for key interfaces of LLZO-based solid-state lithium metal batteries. *Mater. Chem. Front.* **8**, 2109–2134 (2024).
- Wang, L. et al. Interfacial engineering for high-performance garnet-based solid-state lithium batteries. *SusMat* **4**, 72–105 (2024).
- Srivastava, P. et al. Interfacial engineering for high-performance garnet-based lithium metal batteries: a perspective on lithiophilicity and lithiophobicity. *EnergyChem* **6**, 100122 (2024).
- Tu, Q., Barroso-Luque, L., Shi, T. & Ceder, G. Electrodeposition and mechanical stability at lithium–solid electrolyte interface during plating in solid-state batteries. *Cell Rep. Phys. Sci.* **1**, 100106 (2020).
- Wang, M. J., Choudhury, R. & Sakamoto, J. Characterizing the Li–solid–electrolyte interface dynamics as a function of stack pressure and current density. *Joule* **3**, 2165–2178 (2019).
- Krauskopf, T., Hartmann, H., Zeier, W. G. & Janek, J. Toward a fundamental understanding of the lithium metal anode in solid-state batteries—an electrochemo-mechanical study on the garnet-type Solid electrolyte  $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ . *ACS Appl. Mater. Interfaces* **11**, 14463–14477 (2019).
- Yan, H. et al. How does the creep stress regulate void formation at the lithium–solid electrolyte interface during stripping? *Adv. Energy Mater.* **12**, 2102283 (2022).
- Barai, P. et al. Study of void formation at the lithium|solid electrolyte interface. *Chem. Mater.* **36**, 2245–2258 (2024).
- Klimpel, M. et al. Assessment of critical stack pressure and temperature in Li–garnet batteries. *Adv. Mater. Interfaces* **11**, 2300948 (2024).
- He, X. et al. Cu-doped alloy layer guiding uniform Li deposition on a Li–LLZO interface under high current density. *ACS Appl. Mater. Interfaces* **13**, 42212–42219 (2021).
- He, M. et al. Formation of self-limited, stable and conductive interfaces between garnet electrolytes and lithium anodes for reversible lithium cycling in solid-state batteries. *J. Mater. Chem. A* **6**, 11463–11470 (2018).
- Fu, K. et al. Transient behavior of the metal interface in lithium metal–garnet batteries. *Angew. Chem. Int. Ed.* **56**, 14942–14947 (2017).
- Krauskopf, T. et al. Diffusion limitation of lithium metal and Li–Mg alloy anodes on LLZO type solid electrolytes as a function of temperature and pressure. *Adv. Energy Mater.* **9**, 1902568 (2019).
- Fu, K. et al. Three-dimensional bilayer garnet solid electrolyte based high energy density lithium metal–sulfur batteries. *Energy Environ. Sci.* **10**, 1568–1575 (2017).
- Han, X. et al. Negating interfacial impedance in garnet-based solid-state Li metal batteries. *Nat. Mater.* **16**, 572–579 (2017).
- Shi, C. et al. All-solid-state garnet type sulfurized polyacrylonitrile/lithium-metal battery enabled by an inorganic lithium conductive salt and a bilayer electrolyte architecture. *ACS Energy Lett.* **8**, 1803–1810 (2023).
- Shi, C. et al. 3D asymmetric bilayer garnet-hybridized high-energy-density lithium–sulfur batteries. *ACS Appl. Mater. Interfaces* **15**, 751–760 (2023).
- Hitz, G. T. et al. High-rate lithium cycling in a scalable trilayer Li–garnet–electrolyte architecture. *Mater. Today* **22**, 50–57 (2019).
- Okur, F. et al. Intermediate-stage sintered LLZO scaffolds for Li–garnet solid-state batteries. *Adv. Energy Mater.* **13**, 2203509 (2023).
- Zhang, H. et al. Bilayer dense-porous  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  membranes for high-performance Li–garnet solid-state batteries. *Adv. Sci.* **10**, 2205821 (2023).
- Zhang, H. et al. Ultrafast-sintered self-standing LLZO membranes for high energy density lithium–garnet solid-state batteries. *Cell Rep. Phys. Sci.* **4**, 101473 (2023).
- Zhang, H. et al. Garnet-based solid-state Li batteries with high-surface-area porous LLZO membranes. *ACS Appl. Mater. Interfaces* **16**, 12353–12362 (2024).
- Kravchik, K. V., Zhang, H., Okur, F. & Kovalenko, M. V. Li–garnet solid-state batteries with LLZO scaffolds. *Acc. Mater. Res.* **3**, 411–415 (2022).

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## Author contributions

K.V.K. and H.Z. wrote the initial draft of the manuscript. H.Z. created the figures. M.V.K. and K.V.K. corrected the manuscript and supervised the project. All authors have given approval to the final version of the manuscript.

## Competing interests

The authors declare no competing interests.

## Additional information

**Correspondence** and requests for materials should be addressed to Kostiantyn V. Kravchik or Maksym V. Kovalenko.

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