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Polymer-based passive layer to stabilize zinc anode in aqueous electrolyte

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	P.L. Taberna
	Patrice Simon
Abstract:	<p>Metallic zinc holds promise as a cost-effective and scalable material for secondary energy storage applications. However, its inherent reversibility issues hinder its practical implementation. Among various strategies, interface engineering has emerged as a promising approach to enhance the reversibility of zinc anodes. Herein we introduce an innovative method involving the parallel deposition of poly(acrylic acid) (PAA) and zinc metal, creating a composite layer of polymer and zinc, denoted as Zn-PAA. This unique Zn-PAA layer deposition technique remarkably enhances interfacial behavior, ensuring superior cyclic stability in symmetric cells. Moreover, the Zn-PAA layer reduces polarization effects and effectively mitigates interface alterations during plating and stripping processes resulting in increased interface stability. This study highlights the potential of simultaneous electropolymerisation and zinc deposition as a promising strategy to coat and densify interface on zinc anode with intertangled matrix of zinc and polymer for improving the performance and stability of zinc anodes in batteries.</p>



December 22th, 2023

Patrice Simon, Professor,
Université Paul Sabatier

Dear Editor,

Please find attached a manuscript entitled “Polymer-based passive layer to stabilize zinc anode in aqueous electrolyte” by Chotard et al., for consideration in *Electrochemistry Communications*.

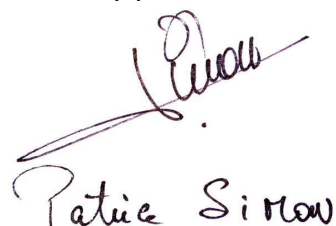
Zinc metal is a promising material for designing batteries for grid storage as Li ion alternatives, due to its abundance, relatively high energy density, and safety. However, use of zinc anodes in rechargeable systems has been hampered by several intrinsic limitations, including Zn dendrites formation on charge, corrosion and passivation.

This paper reports about the electrochemical preparation of an artificial passivation layer (SEI) using acrylic acid as starting monomer to form polyacrylic acid (PAA), using a new method resulting in the co-deposition of a polymer and zinc metal to ensure continuities between the anode and the interface. This unique Zn-PAA layer deposition technique results in the formation of a passive film that remarkably reduces polarization effects and mitigates interface alterations during plating and stripping processes, resulting in increased interface stability.

The manuscript is approved by all the authors for publication and we declare no competing financial interest. I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part.

Hoping that you will suitable this paper for publication in *Electrochemistry Communications*,

Sincerely yours,



Patrice Simon

Editor's Comment: Provide an appropriate graphical abstract that summarises the findings in this work.

Graphical abstract is provided in an attached PowerPoint file.

Reviewer #2

#1: The article by Chotard et al reports passivation of Zn with PAA. The results are interesting and may provide a substantial impact on aqueous Zn-ion batteries. The results provided suggests passivation of Zn based on electrochemical and microscopic analysis. However, without information on the structure, composition, and nano/meso structure of the SEI, the conclusions derived are not sound. I strongly suggest that other conventional analytical results (XRD, IR, SEM, TEM, XPS, etc) be reported to understand the structure of the SEI.

We express our gratitude to the reviewer for providing insightful comments, that we addressed by providing new set of data.

More specifically, we made scanning electron microscopy (SEM) imaging of cross-sections of the solid electrolyte interface (SEI) in conjunction with energy-dispersive X-ray spectroscopy (EDS) analysis for elemental characterizations, and X-ray diffraction (XRD) for crystalline phase identification. We also achieved infrared spectroscopy measurements after cycling our electrode to characterize the organic structure of the SEI after cycling. We propose to add the following section to the Supplementary Information section together with corresponding reference in the manuscript (highlighted in the new manuscript provided).

Further characterizations of the Zn-PAA interface.

Scanning electron microscopy (SEM) images presented in Fig. S1a unveil the morphological characteristics of both zinc foil and zinc coated with the electrodeposited solid electrolyte interface (SEI), Zn-PAA. Top view images show a textured surface following the SEI deposition. As expected, the cross-section of the Zn-PAA sample reveals a stark contrast compared to its zinc foil counterpart. While the latter lacks of distinct layer, two distinct regions can be seen on the Zn-PAA sample, in agreement with the deposition of a SEI-like layer on the zinc foil.

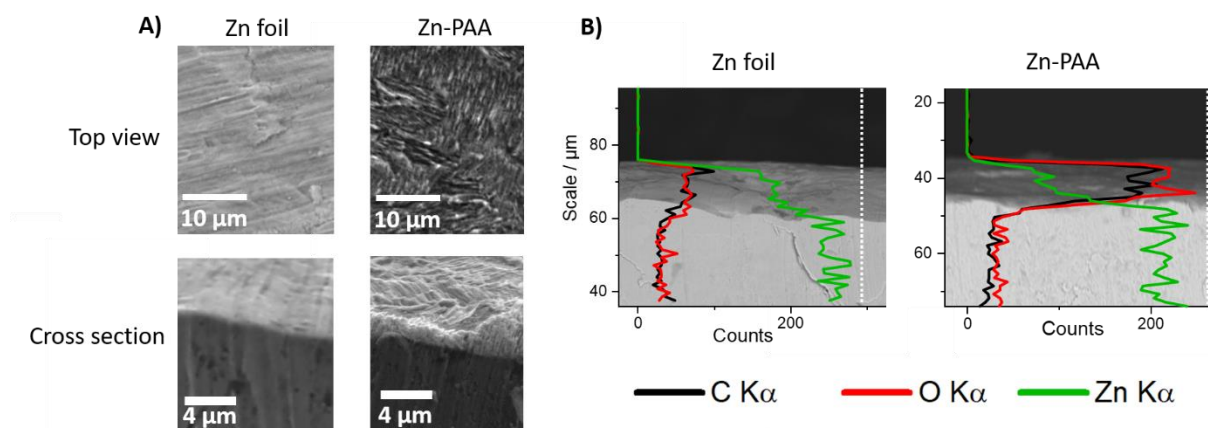


Figure S1. A) SEM images of zinc foil and Zn-PAA top view and cross section. B). EDS characterization of the cross section

Moving further, we used energy-dispersive X-ray spectroscopy (EDS) analysis, specifically focusing on a profile line across the interface (see the white dashed line in Figure S1b). Notably, the EDS profile for the zinc foil sample exhibits minimal fluctuations in the intensity of carbon and oxygen spectral lines as the probe crosses the interface, suggesting an even chemical composition. Conversely, the coated sample displayed a significant increase in both carbon and oxygen intensity at the interface, evidencing the presence of a distinct layer. Such observation well aligns with the results of the infrared spectroscopy measurements presented in Figure 1d of the manuscript. The observed excess in oxygen within the SEI layer can be thus attributed to the presence of carboxylic functional groups within the polymeric component of the SEI, as confirmed by the characteristic vibrational modes identified in the IR spectrum. To further characterize the SEI layer, we conducted grazing-angle X-ray diffraction (XRD) analysis. XRD patterns (Figure S2a) reveal the absence of significant difference in crystalline structure between Zn-PAA and unmodified zinc foil. However, the Zn-PAA sample exhibits a reduced intensity of the (101) peak, suggesting a more favorable textural orientation for zinc plating and stripping processes [1]. Furthermore, the absence of major differences at low angles between the XRD patterns of Zn foil and Zn-PAA suggests that the electrodeposition of the Zn-PAA SEI proceeded without the formation of zinc oxide, hydroxide, or hydroxy sulfate, ensuring a pristine and electrochemically favorable interface.

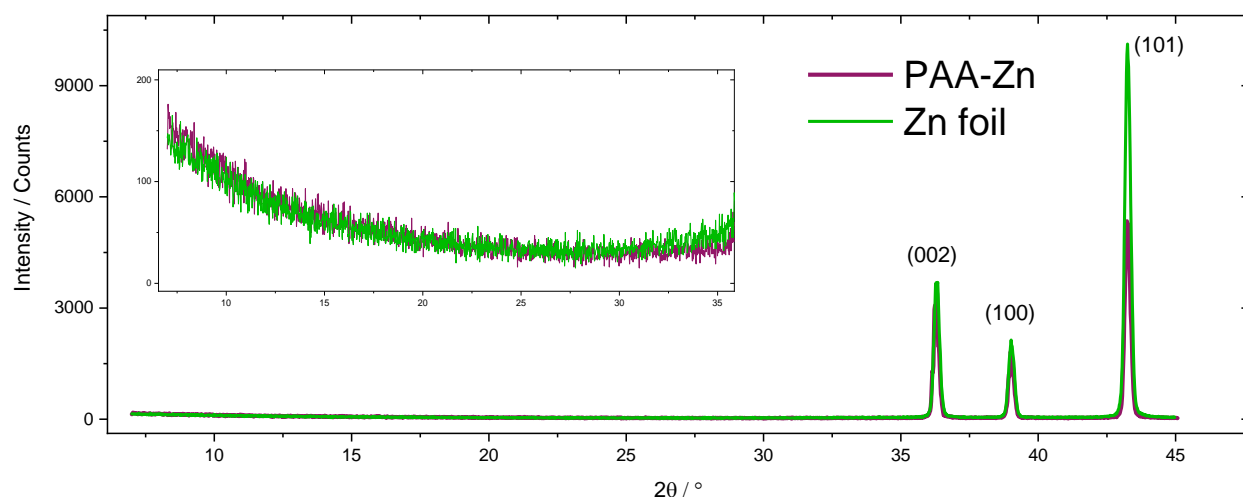


Figure S2. Grazing angle XRD pattern of Zn foil and Zn-PAA. Inset: Zoom at the low angle.

The characterization of the organic structure of the SEI layer was also made after 100 cycles of plating/stripping at a current density of 10 mA.cm^{-2} and a capacity of 0.83 mAh.cm^{-2} , using infrared (IR) spectroscopy. Three main peaks are present in the spectra, at:

- 3300 cm^{-1} : corresponding to the OH functional group, still present after one day (24h) drying at ambient condition.

- 1630 cm^{-1} : this peak, attributed to the C=O stretching vibration coordinated with zinc groups [2], could correspond to carbonyl species interacting with the zinc cations within the SEI. This broad peak might also be convoluted with other peaks corresponding to the free C=O stretching vibration.

- 1075 cm^{-1} : assigned to the C-O vibration further substantiates the presence of organic moieties within the SEI.

In conclusion, comprehensive analysis using SEM, EDS, XRD, and IR tools revealed distinct morphological, elemental, and structural features of the electrodeposited SEI in Zn-PAA. SEM and EDS images clearly show a difference in morphology and composition at the interface while XRD show change in zinc crystallographic texture. Post-cycling IR analysis further confirms the presence of organic moieties within the SEI and provided valuable insights into the functional group structure.

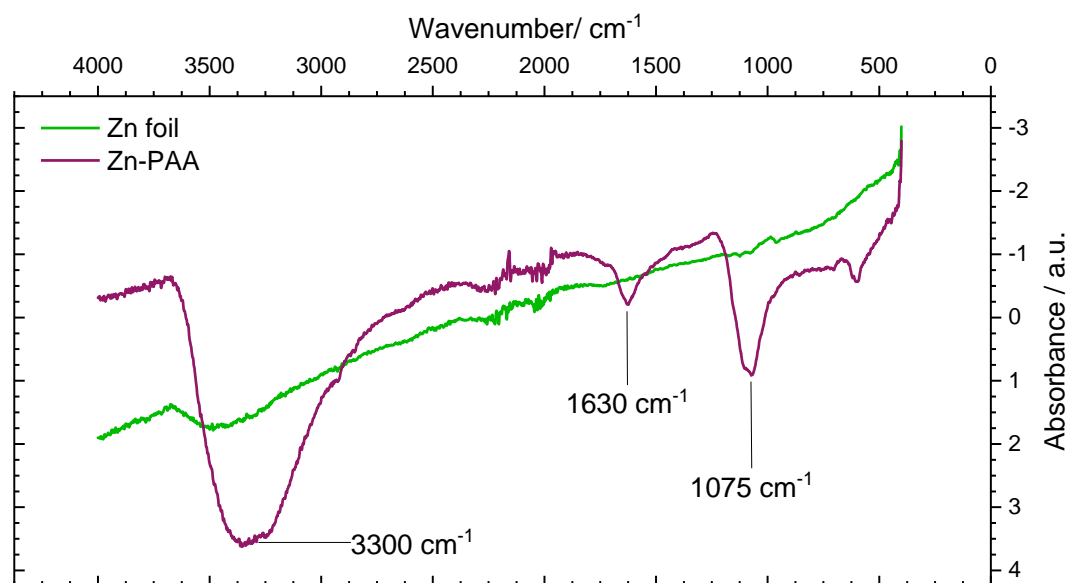


Figure S3: FTIR spectrum of zn foil and Zn-PAA after cycling 100 times at a current density of 10 mA.cm^{-2} and a capacity of 0.83 mAh.cm^{-2} .

Reference

- [1] Z. Chen, J. Zhao, Q. He, M. Li, S. Feng, Y. Wang, D. Yuan, J. Chen, H.N. Alshareef, Y. Ma, Texture Control of Commercial Zn Foils Prolongs Their Reversibility as Aqueous Battery Anodes, *ACS Energy Lett.* 7 (2022) 3564–3571.
<https://doi.org/10.1021/acsenergylett.2c01920>.
- [2] M. Zhu, Q. Zhang, X. Xiao, B. Shi, A novel strategy for enhancing comprehensive properties of polyacrylate coating: Incorporation of highly dispersed zinc ions by using polyacrylic acid as carrier, *Progress in Organic Coatings* 162 (2022) 106596.
<https://doi.org/10.1016/j.porgcoat.2021.106596>.

#2: English is rather poor. Suggest proofreading by an individual proficient in English.

Proofreading has been done, changes are highlighted in the manuscript.

Reviewer #4:

#1: The demonstration of the coordination of Zn^{2+} ions with the PAA carboxylic groups is based on IR measurements. There should be a difference in the IR between free and coordinated carboxylic groups, but only the spectra and peak position are given for the co-deposited layer. The peak positions are matching those of $\text{Zn}(\text{acetate})_2$ (ref 21) but there are differences with IR spectra of PAA coordinating with Zn (Progress in Organic Coatings 162 (2022) 106596). Please comment.

We thank the referee for the comment that gives us the opportunity to clarify this point. As you will see below, both spectra are similar such as explained in the following.

In the paper mentioned by the Referee (Zhu et al), three peaks are assigned. The first peak, located at 1714 cm^{-1} , is attributed to the C=O stretching of the free carboxylic group. We observe a similar peak is at 1734 cm^{-1} , that we assigned as well to the same C=O stretching. The second peak, observed by the authors at 1636 cm^{-1} , is attributed to carboxylic groups coordinated with Zn^{2+} in a protonated state. Although we did not discuss this peak explicitly as it is only slightly visible in our original Figure, the second derivative analysis of our IR spectra reveals a peak at 1643 cm^{-1} (see Figure S4 below), that we can similarly ascribe to protonated and coordinated carboxylic- Zn^{2+} . The third peak, at 1583 cm^{-1} , is associated by the authors with deprotonated and coordinated versions of carboxylate- Zn^{2+} , which aligns well with our assignment of a peak at 1572 cm^{-1} . To summarize, our infrared spectrum is very similar to the one presented in the work of Zhu et al paper, even if our data are collected in a solid state.

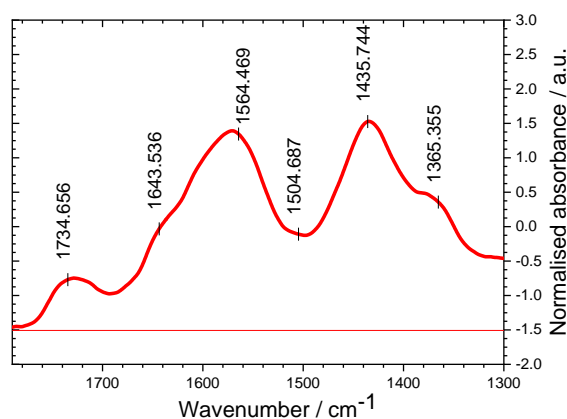


Figure S4: Second derivative analysis of the FTIR spectrum of Fig 1d of the manuscript.

#2: It would be relevant to compare the results obtained with the new approach developed here with those obtained with Zn electrodes modified with the polymer (ex situ polymerisation: Chemical Engineering Journal 462 (2023) 142276.)

We thank the Referee for the comment and apologize if the novelty of our approach was not clearly highlighted.

The paper from Tian et al. (Chemical Engineering Journal, 462, 2023, 142276) reports about the preparation of a stable Zn metal anode by reconstructing its surface with a self-assembled nanoporous polyelectrolytic interlayer prepared by etching bare Zn in aqueous polyacrylic acid (PAA) solutions. Although this deposition method is easy, it does not offer any control on the coating as this is based on an in-situ Zn etching/precipitation process at the rest potential (without polarization). Our approach presents distinct advantages compared to the work of Tian et al. Firstly, our method allows us to control the zinc deposition process by tuning electrochemical conditions, potentially leading to the development of novel and optimized SEI architectures. Our co-deposition technique also offers inherent versatility, enabling the exploration of diverse monomers and additives for further optimization. Then, our discussion goes well beyond the work of Tian et al. by including in-depth electrochemical characterizations using a three-electrode cell which allows for tracking the electrochemical signature of a single Zn electrode. This refined methodology delves deeper into the understanding of interfacial stability, providing valuable insights beyond the scope of the previous work.

#3: On p.9 the authors refer to "discontinuities oscillations". What exactly are those and how to they manifest in Fig 3?

We acknowledge the Referee's comment about the lack of clarity of the terms "discontinuities oscillations." We appreciate their feedback and have rectified the terminology in the figure to accurately reflect the observed phenomenon as "abrupt changes in slope."

As depicted in Figure 3a of the manuscript, these abrupt changes appear during the zinc plating signal. Specifically, two distinct occurrences are identifiable: the first rising at approximately 5.85 hours and the second at around 6.63 hours. Notably, these features become more conspicuous in the derivative plot shown in Figure 4c, that reveals significantly more

noise associated with the zinc foil plating compared to the zinc-PAA plating. Importantly, the observed abrupt changes in slope on this figure correlate to abrupt changes in color.

#4: OCV should refer to cells. When referring to measurements done in three electrode cells, OCP should be used.

Change in the manuscript has been done.

#5: The English is good in general, but many typos and spelling errors remain in the text.

Change in the manuscript has been done.

Urgency statement

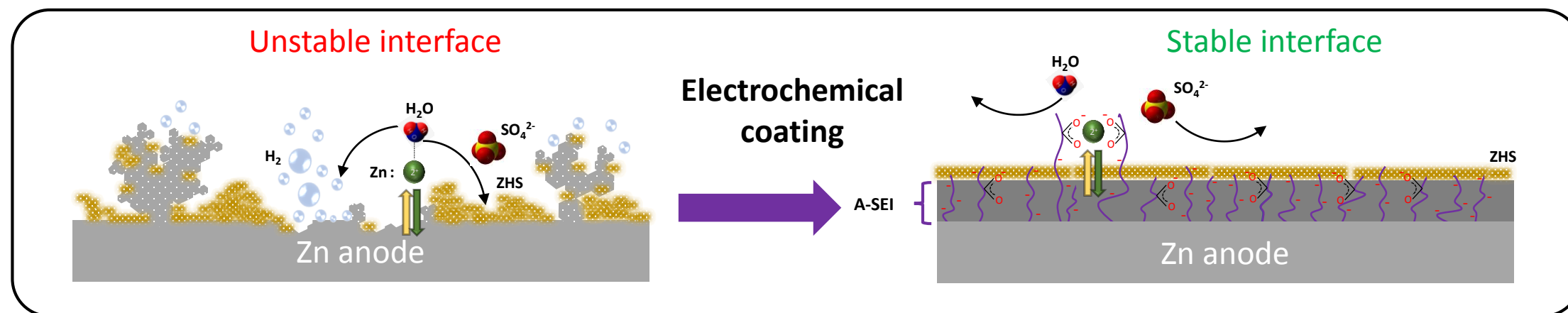
In response to the urgent need for grid energy storage, development of affordable, low environmental footprint, and reversible energy storage solutions are needed. Aqueous-based zinc-ion batteries, thanks to their low cost and safety emerge as promising candidates to meet this demand. However, stabilizing the zinc anode (vs corrosion and Zn dendrites formation on charge) is the key challenge Zn anodes are facing. Our investigation addresses this challenge by introducing a novel coating method that merges electro-polymerization and zinc deposition. The method reported here allows for depositing of both zinc and polymer onto the electrode surface by achieving an electrochemical coating of acrylic acid monomer in the presence of Zn^{2+} onto zinc foil. Cycling tests on symmetric cells on coated Zn anodes revealed enhanced stability vs Zn dendrite growth, and three-electrode test demonstrates the effectiveness of the method in stabilizing the zinc anode interface. This innovative coating method possesses versatility and holds potential for rapid optimization. Currently underexplored in existing literature (to the best of our knowledge), the co-deposition of such films is a pioneering avenue. The encouraging results presented here not only advocate for the development of this method, but also serve as a cornerstone for the development of composite zinc-polymer films, crucial for fortifying the zinc anode coating development.

These findings present a compelling approach to stabilize zinc anode electrodes, offering a promising pathway towards the creation of fully functional secondary cells. This work sets the stage for further exploration and refinement, paving the way for a more resilient and efficient energy storage solution.

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Polymer-based passive layer to stabilize zinc anode in aqueous electrolyte

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Highlights

- Simultaneous zinc deposition and electropolymerisation are realized.
- The deposited interface increases cycling stability.
- Cycling stability is allowed by interface stabilization and reduction of byproducts.

Polymer-based passive layer to stabilize zinc anode in aqueous electrolyte

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Keywords

Zn metal batteries; Interface stabilization; artificial SEI

Abstract

Metallic zinc holds promise as a cost-effective and scalable material for secondary energy storage applications. However, its inherent reversibility issues hinder its practical implementation. Among various strategies, interface engineering has emerged as a promising approach to enhance the reversibility of zinc anodes. Herein we introduce an innovative method involving the parallel deposition of poly(acrylic acid) (PAA) and zinc metal, creating a composite layer of polymer and zinc, denoted as Zn-PAA. This unique Zn-PAA layer deposition technique remarkably enhances interfacial behavior, ensuring superior cyclic stability in symmetric cells. Moreover, the Zn-PAA layer reduces polarization effects and effectively mitigates interface alterations during plating and stripping processes resulting in increased interface stability. This study highlights the potential of simultaneous electropolymerisation and zinc deposition as a promising strategy to coat and densify interface on zinc anode with intertangled matrix of zinc and polymer for improving the performance and stability of zinc anodes in batteries.

1. Introduction

Zinc metal has been used as a battery anode for decades and Zn-based batteries are currently being investigated as a promising material for grid storage due to its abundance, relatively high energy density, and safety [1]. However, widespread adoption of zinc anodes in rechargeable systems has been hampered by several intrinsic limitations, particularly the tendency for Zn dendrites formation on charge (plating stage) together with hydrogen evolution reaction (HER). HER occurs on Zn due to the low redox potential of Zn^{+II} (-0.76 V vs SHE),

despite a low exchange current density for proton reduction on Zn metal (about 10^{-9} A.cm⁻² [2]). HER comes with a local pH increase and current line perturbations both leading to Zn surface heterogeneities; besides, the self-discharge is also correlated to the HER.

Local pH change results in basic zinc salt such as zinc hydroxy sulfate (ZHS) precipitation that further increases electrode polarization and surface heterogeneity [3], leading to the formation and growth of highly reactive Zn dendrites, [4] which further increases the electrochemical active area – as well as HER rates – and ultimately leads to cell failure due to shorting.

To address these interrelated issues, various strategies have been explored [5] such as the design of artificial interfacial layers. These artificial interfacial layers can be made of inorganic or organic materials[6]. The latter is usually obtained from polymers because of their versatility thanks to the diverse array of chemical functionalities they can offer. For instance, polar chemical functionalities have been reported to even the electric field through screening effects[7]. Additionally, the polymer's functional groups have been proven to guide zinc ion flux through coordination, thereby facilitating the energetically demanding desolvation process of Zn[H₂O]₆²⁺ and resulting in smoother plating[8].

Carboxylic function is a promising chemical function for a zinc anode interface as it had been reported to interact more favorably with zinc ions than water, providing an intermediate state for desolvation [9]. Moreover, carboxylic function can coordinate protons thus increasing the hydrogen evolution overpotential [10]. Surface functionalization and electrolyte additives with PAA have previously been shown to improve cycle stability, but these techniques result in an increased overpotential for zinc plating/stripping [9,11]. Surprisingly, direct deposition on the

surface was not compatible with sulfate-based electrolytes[11]. Etching the interface in presence of acrylic acid also seems to be a promising approach[12].

Traditional polymeric a-SEI are mostly deposited by direct method such as spin coating or blade coating and these methods may not be adapted. Indeed, achieving fully conformal coatings on the Zn surface, with uniform thickness and composition remains important challenge [6]. Moreover, they can delaminate during cycling owing to high change in volume of the zinc anode, resulting in an interspace between the as deposited layer and thus lose its protective effect[13].

In this work, we develop an artificial SEI (a-SEI) using acrylic acid as starting monomer to form polyacrylic acid (PAA). We propose a new method to coat and densify interface on zinc anode with intertangled matrix of polymer and zinc metal to ensure continuities between the anode and the interface. Co-deposition of zinc and functional molecules (such as PAA) for protection of zinc anode is a new strategy that has been barely touched in the literature[14]. PAA coating is prepared by radical polymerization of the acrylic acid under cathodic polarization in aqueous media[15]. Simultaneously zinc is also plated at high current density which is expected to promote a favorable texture of the zinc [16]. We show that our method of coating leads to the stabilization of zinc anode interface.

2. Material and methods

2.1 Preparation of Zn-PAA interface

Zinc foil, 250 μm thick, 99.98% purity (thermo scientific) was used as working electrode. The coating solution consists of 5.77 g of ZnSO_4 (98%, thermo scientific), 0.8 g of ZnO (99.5 %

across organics) and 3 ml of acrylic acid (98 % Thermo scientific). Before each deposition oxygen is purged by bubbling of nitrogen in the solution for 5 min. Cyclic voltammetry at 50 mV.s⁻¹ is used to deposit zinc and initiate polymerization of the monomer. Electrode is first polarized to +1.6 V vs Ag/AgCl to get a clean and etched surface. Deposition is then achieved by 11 zinc plating and stripping cycles, between -1.6 V and -0.4 V vs Ag/AgCl. After coating, the electrodes were rinsed with DI water and carefully dried with N₂.

2.2 Characterization

SEM imaging was made from a Vega 3 instruments from Tescan with Oxford X-MAX EDS detector (50 mm²). Fourier-transform infrared spectroscopy, in conjunction with attenuated total reflection, was used to record infrared spectra in a Thermo Scientific Nicolet model 6700 FT-IR spectrometer between 4000 and 400 cm⁻¹. Contact angle measurement was made from DSA30 Drop Shape Analyzer from Kruss. Microscope 3D imaging was made on a Keyence microscope with VH-Z100R objective. XRD at a grazing angle of 1° were realized on a Bruker D8 Advance.

2.3 Electrochemical measurements

Symmetric tests were run in coin-cells (CR 2032). GFA separator was used in combination with two coated or uncoated zinc disc. 100 µL of electrolyte (2M ZnSO₄ + 0.3 M MnSO₄) was dropped on 16 mm GFA glass fiber separator. Test was run on LAHNE M340A battery cycler. For 3 Electrode cell Swagelok were used flooded with 2 M ZnSO₄+ 0.3 M MnSO₄ electrolyte and GFB glass fiber separator was used. Biologic VSP-300 was used to perform electrochemical tests. For three electrode cell, IR drop is measured and subtracted.

3. Results and discussion

3.1 Characterization of Zn-PAA Artificial Layer

Fig. 1a shows the charge exchanged during the cyclic voltammetry to grant a coating on the zinc foil. Fig. 1b presents SEM images of the zinc surface before and after coating. The coated electrode surface (Zn-PAA) exhibits minimal changes after coating, primarily due to the zinc deposit, which appears non-porous at the micron scale. However, a subtle micropatterning is evident on the surface. The SEM image clearly demonstrates the deposition of zinc during the electrochemical coating process, thanks to the presence of Zn^{+II} ions in the electrolyte. Further SEM images of the samples' cross section (Fig. S1a) unveil the interface patterning due to Zn-PAA interface and energy-dispersive X-ray spectroscopy provides evidence that the interface is rich in carbon and oxygen (Fig. S1b). Following the deposition, contact angle measurements with 20 μL of 2M ZnSO_4 + 0.3M MnSO_4 were performed and are presented in Fig. 1c. Zn-PAA exhibits a significantly lower contact angle compared to untreated Zn foil ($\sim 95^\circ$ vs. $\sim 50^\circ$). This observation indicates a favorable interaction between the electrolyte and Zn-PAA, which can be attributed to the hydrophilic polar surface groups introduced by the coating [17]. These polar groups embedded within the zinc framework effectively reduce the interfacial free energy between zinc and the electrolyte, promoting uniform zinc nucleation by increasing the number of stable nuclei [18,19], therefore it is expected to affect significantly the plating polarization[20]. A side effect of this higher hydrophilicity is that $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ may desolvate more easily prior to plating, lowering the potential polarization.

To further assess the surface modification, Fourier transform infrared (FTIR) spectroscopy was carried out on bare zinc foil and on the treated zinc foil. The FTIR spectrum (Fig. 1c) of the bare zinc foil exhibits no significant peaks, whereas the treated Zn foil's spectrum reveals two high intensity peaks, at 1572 and 1435 cm^{-1} , which corresponds to the antisymmetric and symmetric

stretching vibrations of the carboxylate group (COO^-), respectively[21,22]. The presence of these two characteristic carboxylate (COO^-) absorption bands, and a weak C=O band at 1726 cm^{-1} suggests that a significant part of the initial carboxylic acid groups have coordinated with zinc ions. Grazing angle XRD (Fig S2) reveals the absence of significant disparities in crystalline structure between Zn-PAA and unmodified zinc foil.

According to these findings, the artificial interface layer is likely facilitating $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ desolvation prior to the plating as water interacts with the polymeric interface layer's backbone via the pending carboxylate groups.

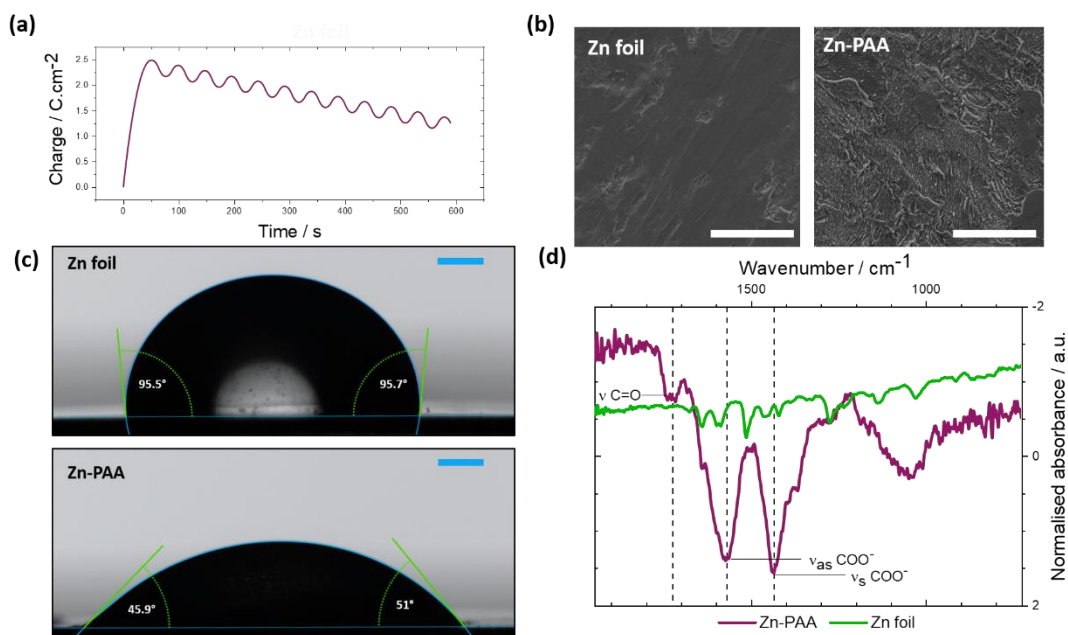


Figure 1: Characterization and deposition of the Zn-PAA interface. (a) Charge exchanged during coating (b) SEM images of the zinc anode surface before (left) and after (right) deposition of the Zn-PAA interface layer, scalbar is $50\text{ }\mu\text{m}$. (c) Contact angle measurement on pristine zinc foil (top) and on Zn-PAA coated anode (bottom), scalbar is 1 mm . (d) FTIR spectrum of zn foil and Zn-PAA

3.2 Zn-PAA||ZnPAA and Zn||Zn symmetric cell's electrochemical stability

To observe whether or not the artificial interface brings in any extra electrochemical stability, symmetric cells were assembled and tested under high current density conditions (10 mA cm^{-2}) and moderate capacity (0.83 mAh cm^{-2}) - 0.3 M MnSO_4 is added to the electrolyte to stick with actual electrolyte formulation used in regular full cells and to limit Mn^{2+} dissolution from MnO_2 during cycling of full cell [23,24]. In Fig.2 are compared the results obtained for a Zn||Zn symmetric cell and for a Zn-PAA||Zn-PAA symmetric cell. As noticed in Fig. 2a, the control cell (Zn||Zn symmetric cell, green curve) failed after 95 hours: a steep increase in cell polarization is observed only after 70 hours of cycling. This sudden cell voltage rise is assumed to be due to the precipitation of uncontrolled basic zinc salts (ZHS) on the electrode surface causing electrode passivation. These potential fluctuations are in line with the finding of Kazemian et al [25] that pointed out the local precipitation of zincate species ruled by local alkalinity in weakly acidic electrolyte inducing mesoscopic inhomogeneities. These reactions are accompanied with electrolyte decomposition and consumption [19]. In contrast, the Zn-PAA cell exhibits a decent potential polarization stability for more than 900h of cycling. According to those findings, the interface layer is likely preventing the uncontrolled basic zinc salt precipitation (ZHS) and/or dendritic growth, keeping the potential polarization low. As illustrated in Fig. 2b, the cell voltage of the Zn-PAA||Zn-PAA cell was lower than that of the Zn||Zn cell during the first cycles, as a value of 46 mV was measured and 65 mV, respectively. It is worth noting that even after prolonged cycling, the Zn-PAA||Zn-PAA cell voltage is kept low and constant ($\pm 70 \text{ mV}$) during plating and stripping, indicating its resistance to short circuit (Fig. 2c)[26]. This lower cell voltage upon cycling, and its resulting extended cell lifespan, underscore the significant enhancement in zinc anode stability achieved through the designed artificial interface.

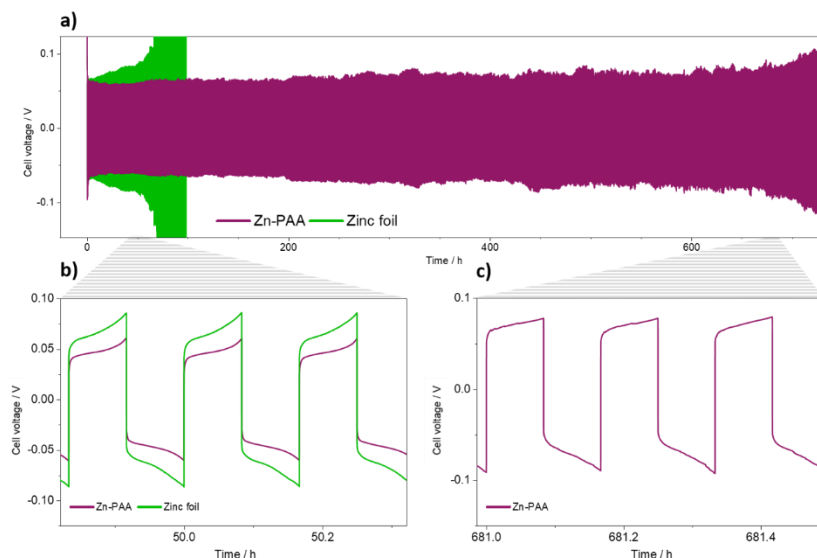


Figure 2: Long term stability of Zn-PAA coating by symmetric cell testing. (a) Cell voltage of Zn||Zn cell and Zn-PAA||Zn-PAA cell. (b) Zoom on cell voltage at 50h. (c) Zoom on cell voltage at 681 h.

Although it is promising, as it is symmetric two-electrode cells, it is not possible to clearly assign what is more affected by the interface modification: the Zn plating or the Zn stripping or the both? To gain a more in-depth understanding of the mechanism underlying the performance enhancement, three-electrode cell tests were employed using mercurous sulfate as reference electrode. It is worth mentioning that the working electrode was consistently stripped first to mimic the initial solicitation in an actual full cell [27]. In Fig. 3a are presented the Zn electrode and Zn-PAA's potential change while applying a constant current of $\pm 10 \text{ mA} \cdot \text{cm}^{-2}$. Three important differences can be seen in the electrochemical behavior of the uncoated and coated Zn foil. First, the observed abrupt change of slope in the uncoated zinc foil potential signal during plating (5.85 h and 6.63h in Fig. 3a) suggests the formation of a mossy-like deposit that detaches and subsequently transforms into dead zinc [28], indicative of dendrite formation. Secondly, it can be noticed that the Zn electrode presents a potential asymmetry between the

stripping regime and the plating one, while a symmetric variation is observed for Zn-PAA electrode. Then, during the cycling, the potential while in stripping phase increases for both electrodes, but the overpotential is higher for the Zn foil compared to the PAA-coated Zn sample. The increase in potential during the stripping phase on Zn electrode is likely associated with the growth of a passivating phase, ZHS, resulting from HER on the electrode surfaces [29]. Interestingly, the Zn stripping is more affected than the Zn plating, although in both cases the overpotential is reduced for Zn-PAA electrode, as compared to Zn electrode. The lower polarization observed for the PAA-coated sample suggests it is less prone to passivation and to dendrite formation. To support this, *ex-situ* microscopy post-cycling in free electrolyte without a separator was performed. It has unveiled localized zinc foil growth with protrusions for zinc foil (Fig. 3b). Zn-PAA coating renders surface homogeneity, averting large-scale localized growth. It is worth noting that after cycling in the same condition, characteristic organic groups are still present at the surface according to IR characterization (Fig S3). This phenomenon is consistent with ZHS phase development, selectively passivating surfaces, which is further supported by continuous impedance monitoring performed at OCP just after electrodes solicitation. Zn foil exhibited a persistent, substantial impedance increase at 100 mHz, indicating an increase in polarization resistance, pointing to ZHS growth (Fig. 3c). In contrast, Zn-PAA displayed a much slower polarization resistance rise, suggesting a reduced ZHS growth and, consequently, a diminished rate of side reactions.

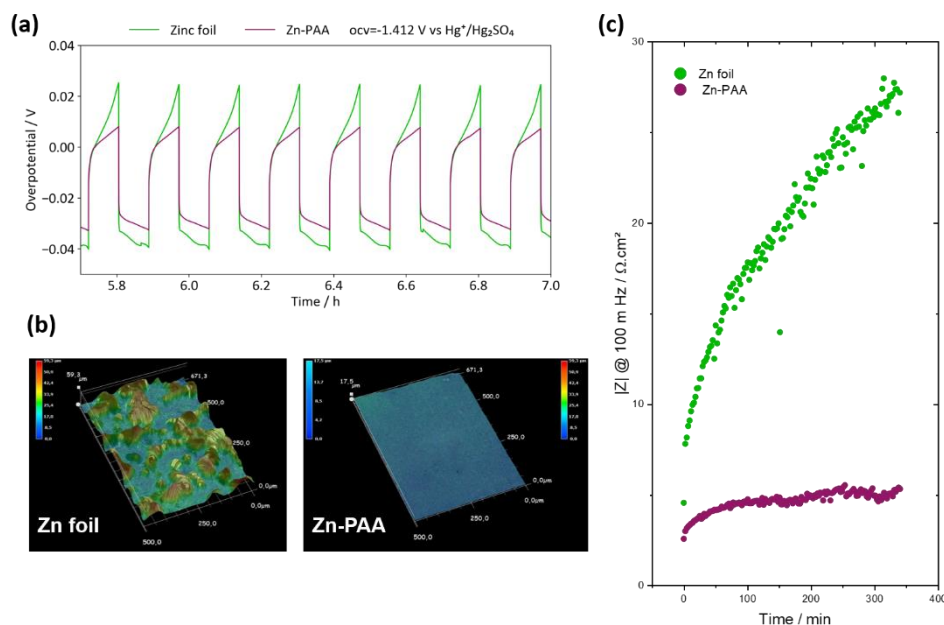


Figure 3: Electrochemical characterization of interface. (a) Chronopotentiometry curves of 3 electrode cell, 10 mA.cm⁻², 0.83 mAh.cm⁻². (b) ex-situ optical microscope image after cycling. (c) Impedance modulus at 100 mHz at OCP vs time.

To gain deeper insights into the electrode signals and the potential variations, the derivative, dV/dQ , was plotted against voltage and cycle number, that is the rate of the potential change (mV.mAh⁻¹) during the galvanostatic cycling presented in Fig. 4. The more yellowish the color is, the greater potential variation relative to charge is important, so a blue color stands for a potential plateau. As shown in Fig. 4 a,b,c,d for both plating and stripping of zinc foil and Zn-PAA, the potential variation rate is important, in line with double layer polarization, followed by a gradual slowdown. During the stripping step, the Zn-PAA electrode exhibits a constant and small increase in potential, while the zinc foil electrode shows a sharp increase, particularly at the end of stripping when the bulk zinc is more susceptible to dissolution (Fig. 4 a,b). This

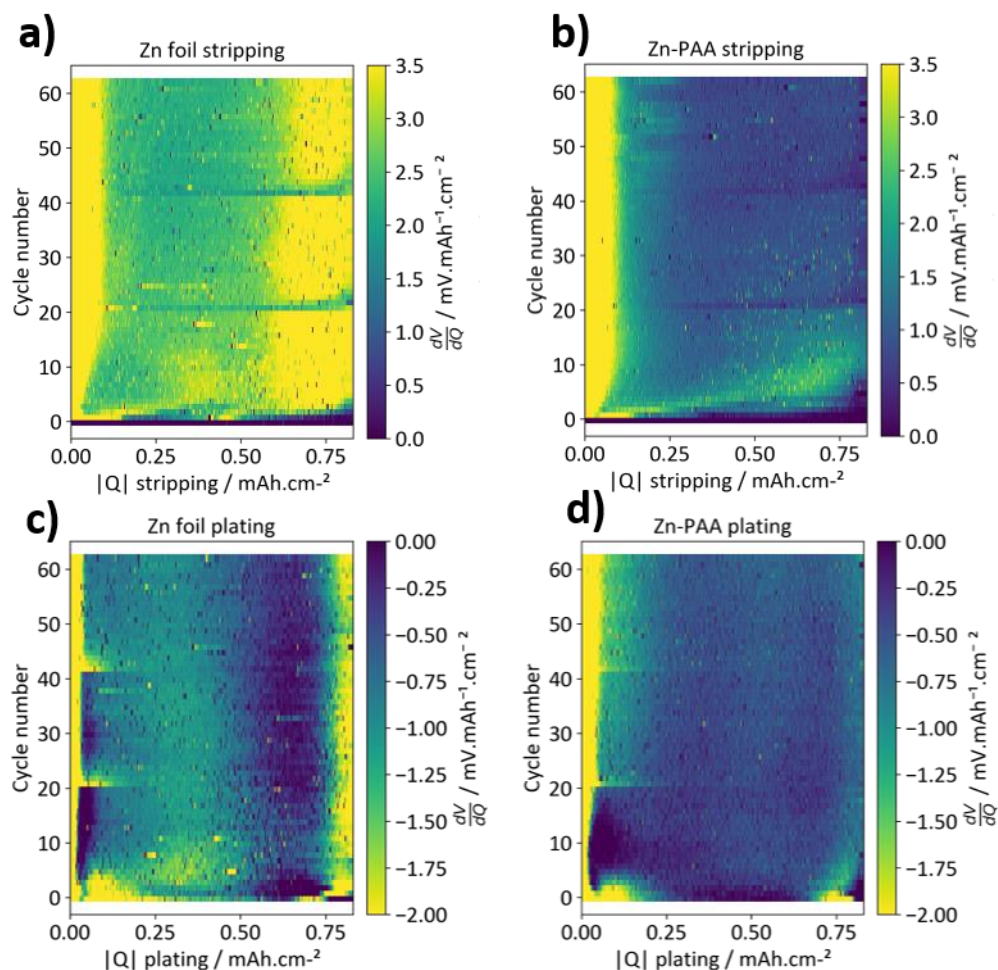


Figure 4: dV/dQ plot. a) dV/dQ plot for zinc foil stripping. b) dV/dQ plot for Zn-PAA stripping. c) dV/dQ plot for zinc foil plating. e) dV/dQ plot for Zn-PAA plating.

difference in behavior suggests that the Zn-PAA interface effectively promotes smoother stripping. For the plating step, the Zn-PAA electrode also exhibits a constant and **small** increase in potential, while the zinc foil electrode shows an abrupt increase in potential at high capacity (Fig. 4 c,d). These observations may suggest **that** the current density is higher for the Zn electrode as compared to Zn-PAA one. As a matter of fact, the interface modification gives rise to a lower surface energy **ensuring** an electrochemical surface area more or less constant under

current for Zn-PAA electrode, oppositely to Zn electrode. Moreover, hydrogen generation is highly likely to occur and might mask a part of Zn electrode's surface, due to its higher surface energy, while the whole Zn-PAA electrode's active surface contact the electrolyte—same assumption can be made for ZHS formation, with bulkier and more heterogeneous deposits for Zn electrode (see Fig. 3b).

To further investigate the interphase changes during cycling, impedance measurements were performed under plating and stripping conditions by polarizing the electrodes at ± 20 mV vs open circuit voltage after 60 galvanostatic (chronopotentiometry) cycles for electrode stabilization.

The Nyquist diagrams shown in Fig. 5 reveal that the impedance of the zinc foil electrode exhibits a negative imaginary part at low frequencies, which is more pronounced for zinc plating. This inductive loop is linked to the variations in resistance, indicating a non-stationary state due to interface instability [30–32]. This observation suggests that the zinc foil electrodes are not stable after several plating/stripping cycles, suggesting a partial passivation of the electrode surface. In contrast, the Zn-PAA electrode does not exhibit this positive imaginary part, indicating that the Zn-PAA interface enhances the stability of the system during plating and stripping. Furthermore, the imaginary part of the Zn-PAA electrode is smaller than that of the zinc foil electrode, suggesting a higher electrode capacitance that could be in line with a larger active electrochemical surface area. Thus, according to those results, the initial electrochemical active surface area is higher for Zn-PAA and the PAA hybrid layer tends to stabilize the interface. The change in $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ desolvation mechanism, the higher wettability and/or the interaction of Zn ions with the pending carboxylate seems to make the interface more stable upon cycling. Nevertheless, an eQCM study is currently under progress to better assess the charge mechanism. It will be the purpose of another following work.

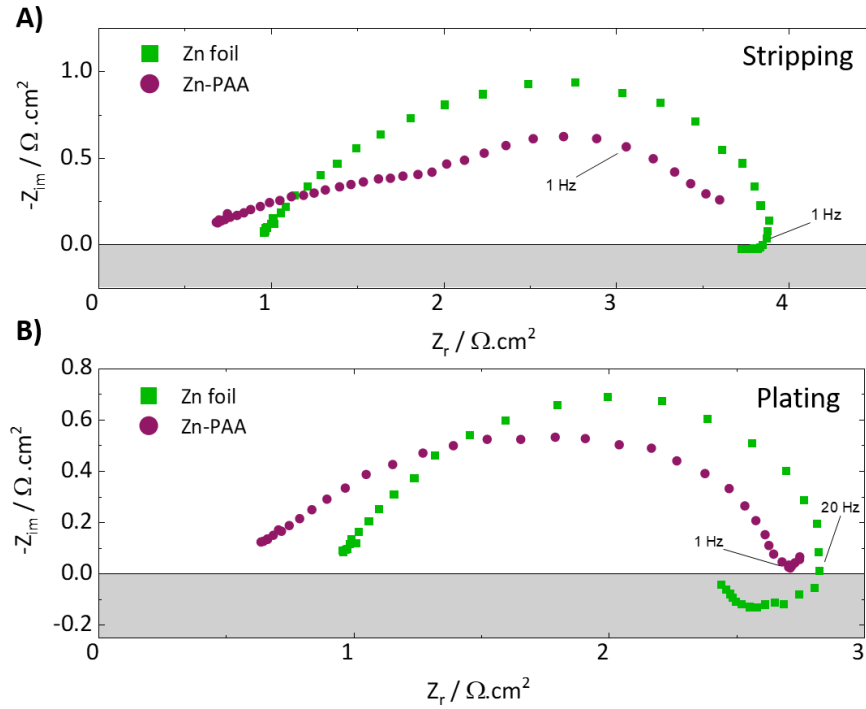


Figure 5: Nyquist diagram of impedance measurement under 20 mV polarization, from 200 kHz to 0.1 Hz. A) Nyquist diagram under stripping of zinc. B) Nyquist diagram under plating of zinc.

4. Conclusion

This study presents a novel method—combining zinc deposition with electropolymerization—to coat an artificial SEI layer on zinc foil. The resulting Zn-PAA interface exhibits an intricately interwoven structure comprising electrodeposited zinc and polymer. Notably, this interface modification significantly reduces the contact angle between anode and electrolyte, and demonstrates enhanced cycling stability. This approach enables smoother plating and stripping processes, resulting in reduced polarization and effective control of surface passivation byproducts facilitating zinc deposition and dissolution while minimizing interface alterations.

These findings underscore the potential of combining electropolymerization with zinc deposition as a promising strategy for improving the stability and performance of zinc anodes in batteries.

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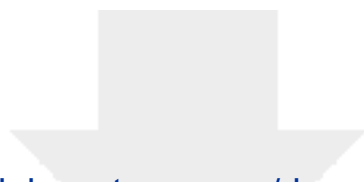
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Reference

- [1] L. Ma, M.A. Schroeder, O. Borodin, T.P. Pollard, M.S. Ding, C. Wang, K. Xu, Realizing high zinc reversibility in rechargeable batteries, *Nat. Energy* 5 (2020) 743–749. <https://doi.org/10.1038/s41560-020-0674-x>.
- [2] N. Perez, ed., *Mixed Potential Theory*, in: *Electrochem. Corros. Sci.*, Kluwer Academic Publishers, Boston, 2004: pp. 155–166. https://doi.org/10.1007/1-4020-7860-9_5.
- [3] T. Zhang, Y. Tang, S. Guo, X. Cao, A. Pan, G. Fang, J. Zhou, S. Liang, Fundamentals and perspectives in developing zinc-ion battery electrolytes: a comprehensive review, *Energy Environ. Sci.* 13 (2020) 4625–4665. <https://doi.org/10.1039/D0EE02620D>.
- [4] Q. Yang, Q. Li, Z. Liu, D. Wang, Y. Guo, X. Li, Y. Tang, H. Li, B. Dong, C. Zhi, Dendrites in Zn- Based Batteries, *Adv. Mater.* 32 (2020) 2001854. <https://doi.org/10.1002/adma.202001854>.
- [5] X. Zhang, J. Hu, N. Fu, W. Zhou, B. Liu, Q. Deng, X. Wu, Comprehensive review on ZINC- ION battery anode: Challenges and strategies, *InfoMat* 4 (2022) e12306. <https://doi.org/10.1002/inf2.12306>.
- [6] L. Ma, C. Zhi, Zn electrode/electrolyte interfaces of Zn batteries: A mini review, *Electrochem. Commun.* 122 (2021) 106898. <https://doi.org/10.1016/j.elecom.2020.106898>.
- [7] J. Xu, H. Li, Y. Jin, D. Zhou, B. Sun, M. Armand, G. Wang, Understanding the Electrical Mechanisms in Aqueous Zinc Metal Batteries: from Electrostatic Interactions to Electric Field Regulation, *Adv. Mater.* (2023) 2309726. <https://doi.org/10.1002/adma.202309726>.
- [8] Z. Guo, L. Fan, L. Wu, B. Li, N. Zhang, Guiding Principles for the Design of Artificial Interface Layer for Zinc Metal Anode, *Batter. Supercaps* 6 (2023) e202200468. <https://doi.org/10.1002/batt.202200468>.
- [9] K. Xie, K. Ren, Q. Wang, Y. Lin, F. Ma, C. Sun, Y. Li, X. Zhao, C. Lai, In situ construction of zinc-rich polymeric solid–electrolyte interface for high-performance zinc anode, *eScience* 3 (2023) 100153. <https://doi.org/10.1016/j.esci.2023.100153>.
- [10] W. Dong, T. Lin, J. Huang, Y. Wang, Z. Zhang, X. Wang, X. Yuan, J. Lin, I.-W. Chen, F. Huang, Electrodes with Electrodeposited Water-excluding Polymer Coating Enable High-Voltage Aqueous Supercapacitors, *Research* 2020 (2020) 2020/4178179. <https://doi.org/10.34133/2020/4178179>.
- [11] C. Huang, W. Deng, X. Yuan, Y. Zhou, C. Li, J. Hu, M. Zhang, J. Zhu, R. Li, Constructing Acrylic-Bonded Stationary Phase as an Artificial SEI for Highly Stable Zn Metal Anodes, *ACS Appl. Mater. Interfaces* 15 (2023) 2341–2350. <https://doi.org/10.1021/acsami.2c16460>.
- [12] S. Tian, L. Zhou, W. He, Y. Tian, Y. Zhou, S. Wu, R. Jian, K.J. Balkus, T. Luo, G. Xiong, A self-assembled nanoporous polyelectrolytic interlayer for highly stable zinc metal anodes, *Chem. Eng. J.* 462 (2023) 142276. <https://doi.org/10.1016/j.cej.2023.142276>.
- [13] Z. Yang, C. Hu, Q. Zhang, T. Wu, C. Xie, H. Wang, Y. Tang, X. Ji, H. Wang, Bulk- Phase Reconstruction Enables Robust Zinc Metal Anodes for Aqueous Zinc- Ion Batteries, *Angew. Chem. Int. Ed.* (2023) e202308017. <https://doi.org/10.1002/anie.202308017>.
- [14] Q. Wang, J. Zhao, J. Zhang, X. Xue, M. Li, Z. Sui, X. Zhang, W. Zhang, C. Lu, Dendrite-Free Zn/rGO@CC Composite Anodes Constructed by One- Step Co- Electrodeposition for Flexible and High- Performance Zn- Ion Batteries, *Adv. Funct. Mater.* (2023) 2306346. <https://doi.org/10.1002/adfm.202306346>.

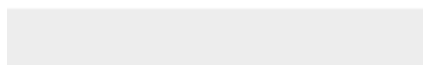
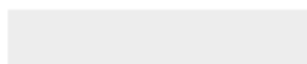
- [15] D. Meinderink, A.G. Orive, G. Grundmeier, Electrodeposition of poly(acrylic acid) on stainless steel with enhanced adhesion properties, *Surf. Interface Anal.* 50 (2018) 1224–1229. <https://doi.org/10.1002/sia.6440>.
- [16] W. Yuan, X. Nie, G. Ma, M. Liu, Y. Wang, S. Shen, N. Zhang, Realizing Textured Zinc Metal Anodes through Regulating Electrodeposition Current for Aqueous Zinc Batteries, *Angew. Chem.* 135 (2023) e202218386. <https://doi.org/10.1002/ange.202218386>.
- [17] H. Du, R. Zhao, Y. Yang, Z. Liu, L. Qie, Y. Huang, High- Capacity and Long- Life Zinc Electrodeposition Enabled by a Self- Healable and Desolvation Shield for Aqueous Zinc-Ion Batteries, *Angew. Chem. Int. Ed.* 61 (2022) e202114789. <https://doi.org/10.1002/anie.202114789>.
- [18] T. Wang, P. Wang, L. Pan, Z. He, L. Dai, L. Wang, S. Liu, S.C. Jun, B. Lu, S. Liang, J. Zhou, Stabling Zinc Metal Anode with Polydopamine Regulation through Dual Effects of Fast Desolvation and Ion Confinement, *Adv. Energy Mater.* 13 (2023) 2203523. <https://doi.org/10.1002/aenm.202203523>.
- [19] Z. Zhao, J. Zhao, Z. Hu, J. Li, J. Li, Y. Zhang, C. Wang, G. Cui, Long-life and deeply rechargeable aqueous Zn anodes enabled by a multifunctional brightener-inspired interphase, *Energy Environ. Sci.* 12 (2019) 1938–1949. <https://doi.org/10.1039/C9EE00596J>.
- [20] J. Hao, X. Li, S. Zhang, F. Yang, X. Zeng, S. Zhang, G. Bo, C. Wang, Z. Guo, Designing Dendrite- Free Zinc Anodes for Advanced Aqueous Zinc Batteries, *Adv. Funct. Mater.* 30 (2020) 2001263. <https://doi.org/10.1002/adfm.202001263>.
- [21] Y. Zhang, F. Zhu, J. Zhang, L. Xia, Converting Layered Zinc Acetate Nanobelts to One-dimensional Structured ZnO Nanoparticle Aggregates and their Photocatalytic Activity, *Nanoscale Res. Lett.* 3 (2008) 201. <https://doi.org/10.1007/s11671-008-9136-2>.
- [22] T. Ishioka, Y. Shibata, M. Takahashi, I. Kanesaka, Y. Kitagawa, K. T. Nakamura, Vibrational spectra and structures of zinc carboxylates I. Zinc acetate dihydrate, *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* 54 (1998) 1827–1835. [https://doi.org/10.1016/S1386-1425\(98\)00063-8](https://doi.org/10.1016/S1386-1425(98)00063-8).
- [23] Z. Li, Y. Li, X. Ren, Y. Zhao, Z. Ren, Z. Yao, W. Zhang, H. Xu, Z. Wang, N. Zhang, Y. Gu, X. Li, D. Zhu, J. Zou, Elucidating the Reaction Mechanism of Mn^{2+} Electrolyte Additives in Aqueous Zinc Batteries, *Small* 19 (2023) 2301770. <https://doi.org/10.1002/smll.202301770>.
- [24] I. Aguilar, P. Lemaire, N. Ayouni, E. Bendadesse, A.V. Morozov, O. Sel, V. Balland, B. Limoges, A.M. Abakumov, E. Raymundo-Piñero, A. Slodczyk, A. Canizarès, D. Larcher, J.-M. Tarascon, Identifying interfacial mechanisms limitations within aqueous Zn-MnO₂ batteries and means to cure them with additives, *Energy Storage Mater.* 53 (2022) 238–253. <https://doi.org/10.1016/j.ensm.2022.08.043>.
- [25] M. Kazemian, F. Rossi, A. Casaroli, T. Caielli, B. Kaulich, M. Kiskinova, I. Sgura, B. Bozzini, X-ray imaging and micro-spectroscopy unravel the role of zincate and zinc oxide in the cycling of zinc anodes in mildly acidic aqueous electrolytes, *J. Power Sources* 524 (2022) 231063. <https://doi.org/10.1016/j.jpowsour.2022.231063>.
- [26] Q. Li, A. Chen, D. Wang, Z. Pei, C. Zhi, “Soft Shorts” Hidden in Zinc Metal Anode Research, *Joule* 6 (2022) 273–279. <https://doi.org/10.1016/j.joule.2021.12.009>.
- [27] Q. Li, A. Chen, D. Wang, Y. Zhao, X. Wang, X. Jin, B. Xiong, C. Zhi, Tailoring the metal electrode morphology via electrochemical protocol optimization for long-lasting aqueous zinc batteries, *Nat. Commun.* 13 (2022) 3699. <https://doi.org/10.1038/s41467-022-31461-7>.

- [28] Y. Wang, Y. Chen, W. Liu, X. Ni, P. Qing, Q. Zhao, W. Wei, X. Ji, J. Ma, L. Chen, Uniform and dendrite-free zinc deposition enabled by *in situ* formed AgZn₃ for the zinc metal anode, J. Mater. Chem. A 9 (2021) 8452–8461.
<https://doi.org/10.1039/D0TA12177K>.
- [29] W. Lim, X. Li, D. Reed, Understanding the Role of Zinc Hydroxide Sulfate and its Analogues in Mildly Acidic Aqueous Zinc Batteries: A Review, Small Methods (2023) 2300965. <https://doi.org/10.1002/smt.202300965>.
- [30] L. Wang, D. Snihirova, M.D. Havigh, M. Deng, S.V. Lamaka, H. Terryn, M.L. Zheludkevich, Non-stationarity in electrochemical impedance measurement of Mg-based materials in aqueous media, Electrochimica Acta 468 (2023) 143140.
<https://doi.org/10.1016/j.electacta.2023.143140>.
- [31] H. Brandstätter, I. Hanzu, M. Wilkening, Myth and Reality about the Origin of Inductive Loops in Impedance Spectra of Lithium-Ion Electrodes — A Critical Experimental Approach, Electrochimica Acta 207 (2016) 218–223.
<https://doi.org/10.1016/j.electacta.2016.03.126>.
- [32] D. Klotz, Negative capacitance or inductive loop? – A general assessment of a common low frequency impedance feature, Electrochem. Commun. 98 (2019) 58–62.
<https://doi.org/10.1016/j.elecom.2018.11.017>.



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