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Minimizing Interfacial Resistance between Polymer Electrolytes and Metal Electrodes using Applied Current

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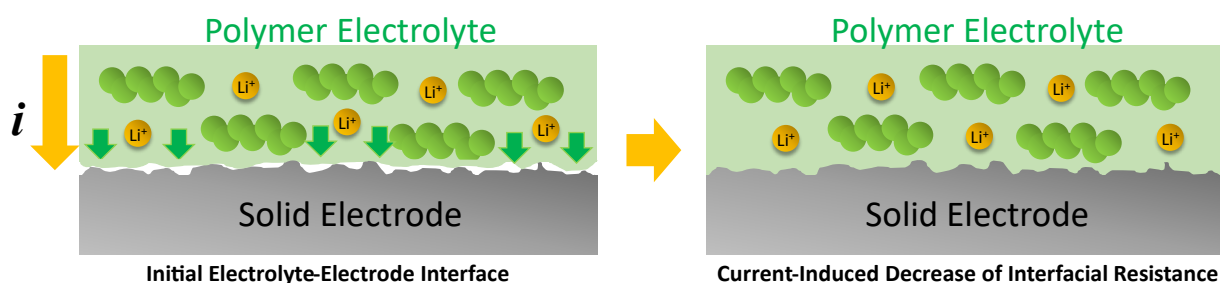
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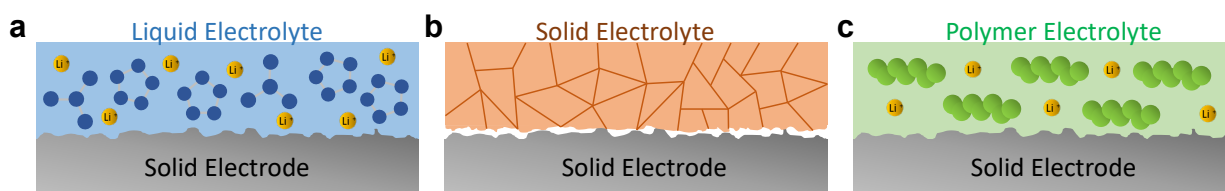
Abstract

Reducing the interfacial resistance between different phases in electrochemical systems is crucial for enabling practical applications. In this work, we proposed a process for reducing the interfacial resistance between polymer electrolytes and metal electrodes. Thus far in the literature, the lowest interfacial resistance reported in these systems is $15 \text{ } \Omega \cdot \text{cm}^2$. In this study, assembled and preconditioned symmetric cells with lithium-indium alloy electrodes showed similar values. The current through the cell was increased in steps up to the limiting current. This resulted in a permanent decrease of the interfacial resistance to values as low as $1 \text{ } \Omega \cdot \text{cm}^2$, a value that is comparable to that of optimized lithium-ion batteries. The proposed process is general and it could be applied to any combination of polymer electrolytes and metal electrodes.

TOC



There is continuing interest in the development of all-solid rechargeable lithium batteries with high energy density.¹⁻⁵ Recent interest in this field has been sparked by the discovery of inorganic solid electrolytes with conductivity that is comparable to liquid electrolytes.⁶⁻⁹ An underappreciated difference between conventional lithium-ion batteries and all-solid lithium batteries is the nature of contact between the electrodes and the electrolyte.^{10,11} All solid materials possess inherent surface roughness that is neither controlled nor quantified. It is obvious that ion transport between the electrolyte and the electrode can only occur if the electrolyte fills the microscopic crevices that are present in the electrode. This occurs readily in the case of liquid electrolytes because the molecules and ions are free to enter the crevices (assuming that the liquid wet the solid electrode). This is shown schematically in **Scheme 1a**. In the case of hard solid electrolytes, filling the crevices between the electrolyte and electrode is nontrivial as shown in **Scheme 1b**. Deformable polymer electrolytes may, in principle, fill the crevices in the electrode as shown in **Scheme 1c**, but the deformation energy in these systems is finite. To our knowledge, the processes needed to obtain intimate contact between polymer electrolytes and electrodes have not yet been established. Our objective is to describe such a process.



Scheme 1. Schematics of the interface between different kinds of electrolytes and a solid electrode with surface roughness. (a) liquid electrolyte, (b) undeformable hard solid electrolyte, and (c) deformable polymer electrolyte. We hypothesize that perfect adhesion between the polymer electrolyte and the electrode can be achieved if the polymer can be driven into the crevices.

The nature of electrolyte-electrode contact can be gauged from measurements of interfacial resistance. Interpretation of these measurements in terms of a microscopic model is convoluted because of the emergence of interfacial layers such as solid electrolyte interphase (SEI). In spite of this, the interfacial resistance between liquid electrolytes and lithium metal electrodes ranges between 10 and 100 $\Omega\cdot\text{cm}^2$.¹²⁻¹⁴ In an important study, Sharafi et al.¹⁵ measured the interfacial resistance between a hard solid electrolyte, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), and lithium metal. The untreated interfacial resistance was 400 $\Omega\cdot\text{cm}^2$. However, the removal of surface contaminants, LiCO_3 and LiOH , resulted in interfacial resistance of 2 $\Omega\cdot\text{cm}^2$. All other papers report values higher than 10 $\Omega\cdot\text{cm}^2$.¹⁶⁻¹⁹

Significantly less work has been done on the interfacial resistance between polymer electrolytes and solid electrodes. In the case of hard solid electrolytes, surface contaminants created during the synthesis will remain there after cell assembly. This is not the case for liquid and polymer electrolytes. In these cases, there is no control over the particular electrolyte molecules that contact the electrodes. It should be clear that methodologies for reducing interfacial resistance in hard solid electrolytes cannot be applied to liquid and polymer electrolytes. Values ranging between 15 and 500 $\Omega\cdot\text{cm}^2$ have been reported for the interfacial resistance between lithium metal and mixtures of poly(ethylene oxide) (PEO) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI).²⁰⁻²² These values reflect the resistance and instability of the SEI layer. In this paper, we study the interface between lithium-indium alloy electrodes and polymer electrolytes. We found a systematic reduction in interfacial resistance as a function of applied current density. Using this process, we obtained interfacial resistances as low as 1 $\Omega\cdot\text{cm}^2$. We posit that the applied current drives the polymer electrolytes^{23,24} into the crevices on the surface of the electrode.

Two different polymer electrolytes were prepared by (1) mixing PEO with number averaged molecular weight of 275 kg/mol with LiTFSI, PEO/LiTFSI, and (2) mixing poly(pentyl malonate)(PPM) with number averaged molecular weight of 26 kg/mol with LiTFSI, PPM/LiTFSI. The electrolytes were placed between two lithium-indium (LiIn) alloy electrodes. The atomic fraction of lithium in the alloy electrode, x_{Li} , was 0.4. The cells were assembled in evacuated pouches. Thus, the stress on the electrode-electrolyte-electrode assembly is 0.1 MPa (1 atm). The cells were operated at 90°C. The salt concentration was specified by the parameter r defined as the molar ratio of lithium to oxygens in each polymer. We focus on results obtained at $r = 0.14$ for PEO/LiTFSI and $r = 0.08$ for PPM/LiTFSI. These are the electrolyte compositions at that support the maximum limiting current at 90°C.²⁵ To ensure a consistent starting point, all cells were conditioned by performing 5 charge/discharge cycles at a low current density of 0.1 mA/cm². Each conditioning cycle consisted of a 3 hour charge, 2 hour rest, followed by a 3 hour discharge, and 2 hour rest. The average interfacial resistance of the PEO/LiTFSI cells was $32 \pm 11 \Omega \cdot \text{cm}^2$. The average interfacial resistance of the PPM/LiTFSI cells was $20 \pm 7 \Omega \cdot \text{cm}^2$.

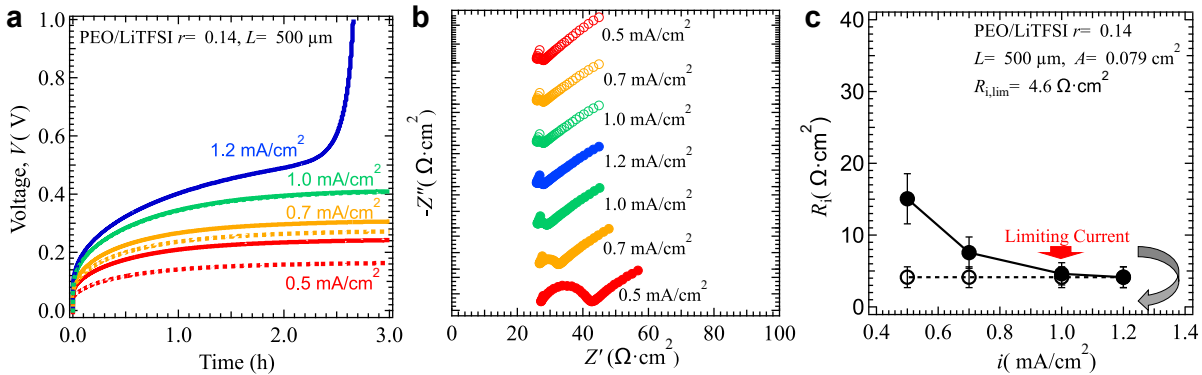


Figure 1. (a) Cell voltage, V , versus time at different applied current densities, i , in a lithium-indium symmetric cell with PEO/LiTFSI electrolytes at $r = 0.14$. Electrolyte thickness (L) is 500 μm . The imposed current density history is a cycle with two sections: a current-increasing section

shown by the solid curves followed by a current-decreasing section shown by dashed curves. Cells were polarized in alternating directions, but the absolute voltage values are shown for clarity. (b) Nyquist plots of imaginary ($-Z''$) versus real (Z') impedance during the current density cycle. (c) Interfacial resistance, R_i , as a function of i during the current density cycle, indicated by the grey arrow. The red arrow represents the limiting current of PEO/LiTFSI electrolytes at $r = 0.14$. Error bars represent the standard deviation of at least three measurements.

The preconditioned cells were then studied as a function of increasing applied current density. **Figure 1a** shows a plot of cell voltage, V , versus time for the PEO/LiTFSI electrolyte with thickness, $L = 500 \mu\text{m}$. The applied current density, i , was gradually increased from 0.5 mA/cm^2 to a value slightly above the limiting current value (1.0 mA/cm^2). At current densities below the limiting current, V approaches a stable value at long times. At $i = 1.2 \text{ mA/cm}^2$, the voltage diverges in accordance with expected behavior above the limiting current.²⁶⁻²⁸ After reaching this point, i was decreased in steps to the lowest applied current density of 0.50 mA/cm^2 . The solid curves in **Figure 1a** correspond to the data obtained when i was increased, while the dashed curves correspond to the data obtained when i was decreased. The solid and dashed curves in **Figure 1a** of the same color thus correspond to the same i . It is clear that V obtained at $i = 0.50 \text{ mA/cm}^2$ during the last step of the experiment is significantly smaller than V obtained during the first step. In other words, the time dependence of V at a given i depends on sample history. The imposed history is a cycle with two sections: a current-increasing section followed by a current-decreasing section.

The cell impedance was measured after each polarization step described above, and the results are shown in **Figure 1b**. After applying $i = 0.5 \text{ mA/cm}^2$ (first step), the measured impedance spectrum is characteristic of an electrolyte studied in a symmetric cell with non-blocking electrodes. The

bulk resistance, R_b , indicated by the start of semicircle is $27 \Omega \cdot \text{cm}^2$, and the interfacial resistance, R_i , indicated by the diameter of semicircle is $16 \Omega \cdot \text{cm}^2$. Increasing i up to 1.2 mA/cm^2 mainly reduces R_i ; R_b remains more-or-less constant. R_i measured at $i = 1.2 \text{ mA/cm}^2$ is $4.6 \Omega \cdot \text{cm}^2$ which is an order of magnitude lower than that of obtained after the first step. Decreasing i step-wise to 0.5 mA/cm^2 changes neither R_b nor R_i . The reason for the history-dependence of the V versus time data at $i = 0.5 \text{ mA/cm}^2$ seen in **Figure 1a** is due to the history-dependence of R_i .

Our results are summarized in **Figure 1c** where R_i is plotted as a function of i . R_i decreases systematically during the current-increasing section of the cycle, but it remains constant during the current-decreasing section of the cycle. It is evident that the process imposed on the cell in **Figure 1** led to a permanent decrease in R_i . The observed behavior in different cells below the limiting current is reproducible, but that above the limiting current is not. For consistency, we report R_i values obtained at or slightly below the limiting current, $R_{i,\text{lim}}$. For the data in **Figure 1c**, $R_{i,\text{lim}}$ is $4.6 \Omega \cdot \text{cm}^2$.

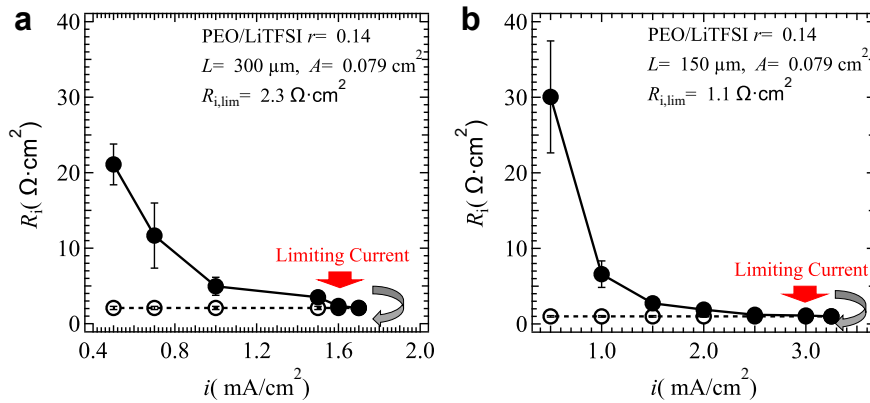


Figure 2. Interfacial resistance, R_i , as a function of applied current density, i , of PEO/LiTFSI electrolytes at $r = 0.14$ with different electrolyte thickness (L), (a) $L = 300 \mu\text{m}$ and (b) $L = 150 \mu\text{m}$, during the current density cycle, indicated by the grey arrow. The red arrow represents the limiting

current of the electrolytes. Error bars represent the standard deviation of at least three measurements.

Since the limiting current is inversely proportional to $L^{29,30}$, we studied the effect of increasing current density on R_i in electrolytes with lower values of L . The results for PEO/LiTFSI with two lower L values (300 μm and 150 μm) are summarized in **Figures 2a** and **2b**, where R_i is plotted as a function of i . Thinner electrolytes allow higher current densities to be applied through the electrolytes. In both cases, R_i decreases systematically during the current-increasing section of the cycle, and it remains constant during the current-decreasing section of the cycle. It is evident that the process imposed on the cells in **Figure 2** led to a permanent decrease in R_i . The electrolyte with $L=150\text{ }\mu\text{m}$ has higher limiting current density and $R_{i,\text{lim}}$ is $1.1\text{ }\Omega\cdot\text{cm}^2$, which is lower than that of the $L=300\text{ }\mu\text{m}$ electrolyte, $2.3\text{ }\Omega\cdot\text{cm}^2$. The absolute value of i is the critical factor for reducing R_i between the metal electrode and electrolyte.

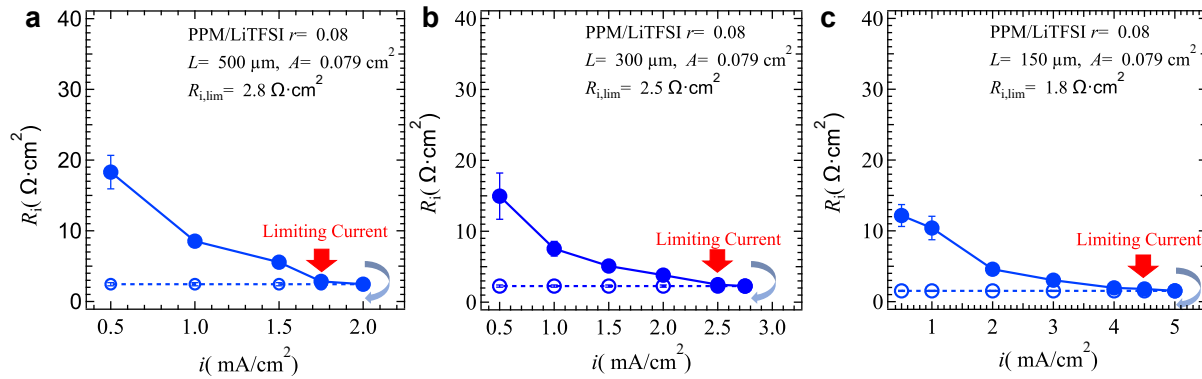


Figure 3. Interfacial resistance, R_i , as a function of applied current densities, i , of PPM/LiTFSI electrolytes at $r = 0.08$ with different electrolyte thickness (L), (a) $L = 500\text{ }\mu\text{m}$, (b) $L = 300\text{ }\mu\text{m}$, and (c) $L = 150\text{ }\mu\text{m}$, during the current density cycle, indicated by the blue arrow. The red arrow represents the limiting current of the electrolytes. Error bars represent the standard deviation of at least three measurements.

In a recent study²⁵, it was shown that PPM/LiTFSI electrolytes have the higher limiting current value than that of PEO/LiTFSI electrolytes. We therefore studied the effect of increasing i on R_i in PPM/LiTFSI electrolytes. Similar to the above-mention study of PEO/LiTFSI electrolytes, symmetric LiIn|PPM/LiTFSI($r = 0.08$)|LiIn cells were assembled and operated at 90°C. Since the limiting current value for PPM/LiTFSI electrolytes at $r = 0.08$ is 1.7 times higher than that of PEO/LiTFSI electrolytes at $r = 0.14$, 1.7 times higher current densities were applied to PPM/LiTFSI electrolytes at $r = 0.08$ (at the same L). **Figure 3** summarizes the results of R_i as a function of i for PPM/LiTFSI electrolytes with three different L , 500 μm , 300 μm , and 150 μm . In all cases, R_i decreases systematically during the current-increasing section of the cycle, but it remains constant during the current-decreasing section of the cycle. As expected, the electrolyte with $L=150 \mu\text{m}$ has $R_{i,\text{lim}} = 1.8 \Omega\cdot\text{cm}^2$, which is lower than that of the $L=500 \mu\text{m}$ electrolyte, $2.8 \Omega\cdot\text{cm}^2$.

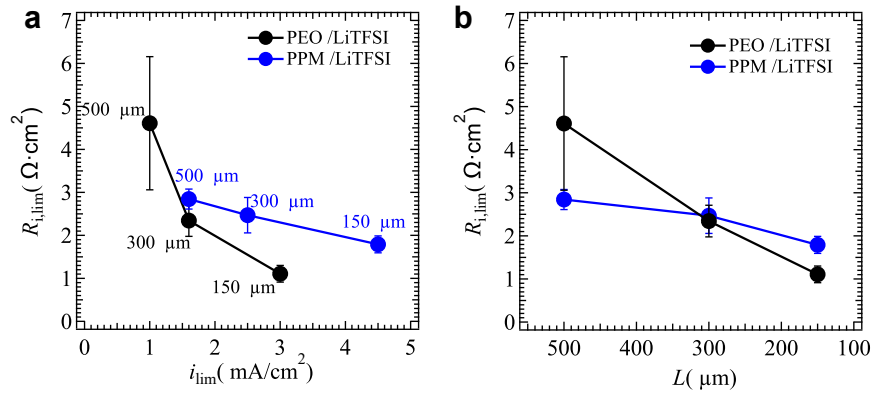


Figure 4. Summary of (a) the interfacial resistance at the limiting current density, $R_{i,\text{lim}}$, as a function of the limiting current, i_{lim} , for PEO/LiTFSI electrolytes at $r = 0.14$ (black) and PPM/LiTFSI electrolytes at $r = 0.08$ (blue) with different electrolyte thickness (L), and (b) $R_{i,\text{lim}}$ as a function of the electrolyte thickness, L . Error bars represent the standard deviation of at least three measurements.

In **Figure 4**, we summarize our results on the extent to which interfacial resistance can be reduced by applied current. In **Figure 4a**, $R_{i,\text{lim}}$ is plotted as a function of the limiting current, i_{lim} , for PEO/LiTFSI and PPM/LiTFSI electrolytes. This figure shows that the reduction in $R_{i,\text{lim}}$ depends not only on the magnitude of the applied current density, but also on the type of polymer electrolyte. $R_{i,\text{lim}}$ of the PEO/LiTFSI electrolyte is a more sensitive function of i . In **Figure 4b** we plot $R_{i,\text{lim}}$ as a function of L for the two electrolytes. For thick electrolytes, applied current has a larger effect in PPM/LiTFSI electrolytes. For thin electrolytes, applied current has a larger effect in PEO/LiTFSI electrolytes. The crossover between these two regimes occurs at $L = 300 \text{ }\mu\text{m}$.

In summary, we have established a new process for reducing R_i between polymer electrolytes and metal electrodes. Current passed through the electrolyte was increased in steps until the limiting current was reached. A permanent reduction of R_i was observed. The underlying phenomena that are responsible for this observation remain to be established. In principle, a reduction in R_i could be due to the removal of surface contaminants or plastic deformation of the electrode.³¹⁻³³ Since polymer electrolytes contain mobile molecules and lithium-indium alloys are essentially rigid³⁴, the reason for the observed reduction in R_i must be different. We hypothesize that the preconditioned interface between polymer electrolytes and metal electrodes contains crevices that prevent intimate contact between the two phases, as shown in **Scheme 1b**. This gives rise to high R_i . The applied current drives the polymer electrolytes into the crevices thereby reducing R_i . For concreteness, we discuss the data in **Figure 2b**, for PEO/LiTFSI with $L = 150 \text{ }\mu\text{m}$. R_i at $i = 0.5 \text{ mA/cm}^2$ is $30 \text{ }\Omega\cdot\text{cm}^2$. However, after increasing the current to the limiting current, R_i reduces to $1 \text{ }\Omega\cdot\text{cm}^2$. Our hypothesis is that in this case, the applied current history increases the contact area between the polymer and the metal electrode by a factor of 30. The height of the crevices is much smaller than the electrolyte thickness and the applied current thus only affects interfacial resistance;

the bulk resistance remains unchanged. Since air gaps of a fraction of a nanometer are sufficient to insulate the two phases locally, proving whether our hypothesis is correct or wrong is nontrivial.

In the highly optimized case of commercial lithium-ion batteries with liquid electrolytes, R_i between the graphite anode and the electrolyte is $1 \text{ } \Omega \cdot \text{cm}^2$. There have been several studies devoted to reducing R_i between lithium metal electrodes and inorganic solid electrolytes.¹⁵⁻¹⁹ The lowest reported R_i is $2 \text{ } \Omega \cdot \text{cm}^2$. Our study suggests that similar values are possible in the case of polymer electrolytes.

Experimental Methods

The salt concentration was specified by the parameter r defined as the molar ratio of lithium to oxygens in PEO and PPM. We prepared two electrolytes, PEO/LiTFSI at $r = 0.14$ and PPM/LiTFSI at $r = 0.08$, following the electrolyte preparation procedure in reference 25. These are the electrolyte compositions that support the maximum limiting current at 90°C .²⁵ The electrolytes were placed between two lithium-indium (LiIn) alloy electrodes (10 mm diameter, 500 μm thickness) with stainless-steel shims (MTI Corporation) separated by a 500, 300, and 150 μm thickness silicon spacer with a 3.175 mm diameter hole. LiIn alloy electrodes were prepared following the procedure in reference 30. The atomic fraction of lithium in the alloy electrode, x_{Li} , was 0.4. Nickel tabs were attached on the stainless-steel shims using Kapton tape and then the cell was vacuum sealed in pouch material, leaving the tab end terminal exposed. Thus, the stress on the electrode-electrolyte-electrode assembly was 0.1 MPa (1 atm). The cells were operated at 90°C . To ensure the formation of uniform solid electrolyte interphase (SEI) layer, all cells were conditioned by performing 5 charge/discharge cycles at a low current density of 0.1 mA/cm^2 . Each

conditioning cycle consisted of a 3 hour charge, 2 hour rest, followed by a 3 hour discharge, and 2 hour rest. Preconditioning was stopped when the voltage response stabilized. Cells were polarized with a constant current density ranging from 0.5 mA/cm² to 5.0 mA/cm² in alternating directions. Each current density was applied until a steady-state potential, V , is recorded. Applied current density was increased until V diverged. After reaching this point, the current density was decreased in steps to the lowest applied current density of 0.50 mA/cm². The cell impedance was measured after each polarization step. The limiting current density was defined as the highest current density at which the steady-state potential could be recorded.

Supporting Information

Typical Nyquist plots before and after the preconditioning cycles.

Conflicts of interest

The authors declare no competing financial interests. The statements, findings, conclusions and recommendations are those of the authors and do not necessarily reflect the U.S. Department of Commerce. Certain commercial equipment, instruments, suppliers and software are identified in this paper to foster understanding.

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