In situ solid-state electrochemistry of mass-selected ions at well-defined electrode–electrolyte interfaces

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Molecular-level understanding of electrochemical processes occurring at electrode–electrolyte interfaces (EEIs) is key to the rational development of high-performance and sustainable electrochemical technologies. This article reports the development and application of solid-state in situ thin-film electrochemical cells to explore redox and catalytic processes occurring at well-defined EEIs generated using soft-landing (SL) of mass- and charge-selected cluster ions. In situ cells with excellent mass-transfer properties are fabricated using carefully designed nanoporous ionic liquid membranes. SL enables deposition of pure active species that are not obtainable with other techniques onto electrode surfaces with precise control over charge state, composition, and kinetic energy. SL is, therefore, demonstrated to be a unique tool for studying fundamental processes occurring at EEIs. Using an aprotic cell, the effect of charge state (PMo12O40(2−)), and the contribution of building blocks of Keggin polyoxometalate (POM) clusters to redox processes are characterized by populating EEIs with POM anions generated by electrospray ionization and gas-phase dissociation. Additionally, a proton-conducting cell has been developed to characterize the oxygen reduction activity of bare Pt clusters (Pt30 ~1 nm diameter), thus demonstrating the capability of the cell for probing catalytic reactions in controlled gaseous environments. By combining the developed in situ electrochemical cell with ion SL we established a versatile method to characterize the EEI in solid-state redox systems and reactive electrochemistry at precisely defined conditions. This capability will advance the molecular-level understanding of processes occurring at EEIs that are critical to many energy-related technologies.

Understanding the intrinsic properties of electroactive species on electrode surfaces is critical to the rational design of stable and efficient electrode–electrolyte interfaces (EEIs) in numerous technologically important solid-state electrochemical systems (1, 2). Performance degradation and instability of electrochemical systems mostly stems from undesired side reactions occurring at EEIs (3). Agglomeration and decomposition of redox-active species in supercapacitors, evolution of resistive lithium metal dendrites at the solid–electrolyte interface in batteries, and dissolution and Ostwald ripening of oxygen reduction reaction (ORR) catalysts such as supported Pt clusters and nanoparticles (NPs) in polymer electrolyte membrane fuel cell (PEMFC) electrodes, are just a few examples of common undesirable processes occurring at EEI that require detailed in situ characterization (3). A fundamental understanding of molecular mechanisms and electrode kinetics is key to the future improvement of the performance of EEIs and the longevity and commercial success of electrochemical technologies. The distribution and adsorption/desorption of counterions on electrode surfaces, and subsequent ion exchange and electron transfer are vital processes that define the complexity of operating EEIs that are currently being studied using in situ and operando characterization as well as high-level computational modeling (4).

Numerous in situ approaches have been developed for simultaneous electrochemical and physical characterization of EEIs (4, 5). Notable examples include magnetic resonance, infrared spectroscopy, photon- and neutron-based scattering approaches, electron microscopy, and the electrochemical quartz crystal microbalance (4, 5). Although there is substantial interest in understanding processes occurring at porous nanostructured solid-state EEIs, the majority of in situ approaches rely on specially designed liquid electrochemical cells. New approaches for studying solid EEIs, therefore, will benefit numerous applications in catalysis, energy conversion, and storage.

The ability to precisely control the presence of ions of interest at solid-state EEIs is essential to understanding their inherent activity. In this study, we report the development of a unique approach that enables in situ electrochemical characterization of ions on a nanostructured solid-state EEI precisely designed using soft-landing (SL) of mass- and charge-selected ions (6–12). Previously, the superior performance of EEIs prepared using SL in comparison with drop casting and electrospray deposition was demonstrated (13). The high specific capacitance and improved stability of EEIs prepared using SL was attributed to the absence of strongly coordinating counterions and uniform deposition of discrete redox-active ions on the electrode. SL efficiently eliminates unwanted contaminants such as inactive counterions and solvent molecules that are commonly present at EEIs prepared using traditional techniques including direct painting, ambient air spray, and electrospray deposition (3). Elimination of strongly coordinating counterions and solvent molecules that alter the distribution and stoichiometry of the compounds of interest at EEI facilitates characterization of the intrinsic activity of precisely defined species.

In situ characterization of kinetics at electrode–electrolyte interfaces (EEIs) is crucial to the rational design of efficient and sustainable solid-state electrochemical technologies. A significant advancement has been made to rationally understand processes at EEIs using solid-state in situ thin-film electrochemical cells fabricated using specially designed ionic liquid membranes with excellent mass-transfer properties. The in situ cells are used to characterize well-defined EEIs generated using ion soft-landing (SL) in controlled environments, both in vacuum and in the presence of reactant gases. Populating EEIs with precisely defined electroactive species using SL facilitates molecular-level understanding of electron transfer processes within deposited species and between species and electrodes, thus providing a powerful methodology to characterize technologically relevant EEIs during operation.

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Significance

In situ characterization of kinetics at electrode–electrolyte interfaces (EEIs) is crucial to the rational design of efficient and sustainable solid-state electrochemical technologies. A significant advancement has been made to rationally understand processes at EEIs using solid-state in situ thin-film electrochemical cells fabricated using specially designed ionic liquid membranes with excellent mass-transfer properties. The in situ cells are used to characterize well-defined EEIs generated using ion soft-landing (SL) in controlled environments, both in vacuum and in the presence of reactant gases. Populating EEIs with precisely defined electroactive species using SL facilitates molecular-level understanding of electron transfer processes within deposited species and between species and electrodes, thus providing a powerful methodology to characterize technologically relevant EEIs during operation.

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In situ electrochemical characterization of soft-landed size-selected metal clusters has been achieved previously by Anderson and coworkers using an elegantly designed in-vacuum liquid electrochemical cell (14, 15). These pioneering studies demonstrated substantial damage of glassy carbon electrodes containing soft-landed Pt clusters upon exposure to air and water, highlighting the importance of characterizing the EEI in vacuum. An approach introduced here is a demonstration of in situ electrochemical studies of precisely selected electroactive species on a solid EEI in a controlled environment. This is achieved by designing and fabricating a solid-state thin-film electrochemical cell that is stable both under vacuum and under controlled gas conditions (gas permeable).

The cell is composed of a porous ionic liquid (IL) membrane on a screen-printed electrode (SPE) (Fig. 1). Due to a wide operating potential range, extremely low vapor pressure, and the absence of side reactions caused by solvent molecules, ILs have been used as state-of-the-art high-performance electrolytes in electrochemical systems such as batteries, supercapacitors, fuel cells, and CO2 conversion catalysts (16–18). For the same reasons, vacuum-based liquid electrochemical cells using ILs have been used for in situ characterization (19). Herein, we introduce solid-state three-electrode electrochemical cells (also known as half-cells) incorporating thin IL membranes for in situ characterization of solid EEIs. Importantly, the in situ electrochemical cell designed using a porous IL membrane mimics the nanostructured electrolyte widely used in many state-of-the-art solid-state electrochemical devices (16).

The in situ cells reported in this study enable (i) characterization of both intrinsic redox and reactive processes with control over the stoichiometry and distribution of analyte species at EEIs in nanostructured solid-state electrolyte under well-controlled conditions and (ii) understanding of the effect of diffusion of ions of interest through pores on their electrochemical activity. Remarkably, it is demonstrated that the rates of diffusion-limited charge-transfer processes in the solid IL membranes are comparable to those observed in liquid electrolytes. In addition, the diffusion of electroactive species in the porous electrolyte layer is similar to that observed in solid-state energy conversion and storage devices (16, 20), thereby emulating technologically relevant mass-transfer conditions.

In redox electrochemistry, Keggin molybdenum polyoxometalate (POM) anions (PMO12O40), stable clusters with multielectron redox activity, are used as a model system. The transfer of up to 24 electrons (e−) was reported for PMO12O40 with retention of its structural integrity making this cluster a promising active material for rechargeable batteries and water electrolyzers (21, 22). SL is used to populate EEIs with different charge states of PMO12O40 (3- and 2-) and complementary fragments of PMO12O40 generated using in-source collision-induced dissociation (CID) to examine the effect on PM redox activity. Reactive electrochemistry experiments (also referred to as catalytic processes) are performed by examining ORR on soft-landed bare Pt cluster ions ~1 nm in diameter produced by magnetron sputtering and gas aggregation. SL of bare metal clusters onto the cell eliminates the need to use stabilizing ligands or solvent molecules that may affect cluster properties, and thus provides a direct route for studying intrinsic electrocatalytic activity. This study is a demonstration of the combination of in situ thin-film electrochemical cells with SL as a versatile approach to explore both the redox and reactive electrochemical processes of selected species at well-defined EEIs, which accurately represents the half-cell conditions of many technologically important electrochemical systems.

Results and Discussion

Characterization of the in Situ Electrochemical Cells

Two types of thin-film electrochemical cells with different IL membranes are developed in this study. Cell 1 is composed of a 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF4)-based aprotic IL membrane with cobaltocene/cobaltocenium (Co/Coc) as an internal reference redox couple (IRRC) on a Pt SPE. Two variants of cell 2 contain (i) an IL membrane prepared using aprotic EMIMBF4 IL and protic trifluoroacetic acid-2-methylpyridine IL, and (ii) a Nafion membrane prepared (using a 5 wt% solution obtained from Sigma-Aldrich) to mimic a conventional PEMFC interface. Both variants of cell 2 are without an IRRC on an indium-tin-oxide (ITO) SPE. The presence of protons in cell 2 makes a nonpolarizable interface at the Ag reference electrode (RE) that acts as a pseudoreference electrode. The formation of a nearly perfect electrochemical double layer (EDL) and efficient diffusion of ions and reactant gases within the in situ cells are important considerations for their design and performance. A detailed description of the development and optimization of the in situ thin-film electrochemical cells is presented in the SI Appendix. Briefly, cyclic voltammetry (CV) of cell 1 indicates (i) a wide operating potential range of ~1,700–1,000 mV vs. Ag (all potential mentioned hereafter are with reference to Ag) (Fig. 2 and SI Appendix, Fig. S1 and S2); (ii) stable rectangular non-Faradaic behavior typical of a 1e− redox process of the IRRC (Co/Coc+) with the formal potential at ~1.480 mV (Fig. 2 and SI Appendix, Fig. S2); (iii) efficient diffusion of ions [diffusion coefficient of (4.9 ± 2.1) × 10−7 cm2/s for Co/Coc+ in EMIMBF4] in the IL membrane as determined by CV of Co/Coc+ at different scan rates (SI Appendix, Fig. S2 and Table S1) using the Randles–Sevčik equation (SI Appendix, Eq. S1). The value of the diffusion coefficient is of the same order of magnitude as values reported in the literature (1.1 × 10−7 cm2/s) for Co/Coc+ in pristine EMIMBF4 (23). It is notable that excellent mass transfer at EEI in solid-state cell 1 is achieved in comparison with liquid electrochemical cells. Furthermore, the diffusion coefficient of ~(6.0 ± 3.2) × 10−7 cm2/s and the Nernst diffusion layer thickness of ~100 nm estimated by analysis of electrochemical impedance spectroscopy (EIS) data obtained with cell 1 (SI Appendix, Fig. S3 A and C and Eqs. S2–S4) are comparable to the values obtained from CV, which corroborates the analysis of the EIS data. The Nernst diffusion layer thickness is well below the total thickness of the IL membrane (~10 µm) determined by scanning electron microscopy (SEM).
CVs of the (i) aprotic in situ cell (cell 1) acquired in two potential ranges in vacuum to represent the redox (Faradaic) behavior of the Ce/Ce+ (IRRC, BPNAS Early Edition) ions were deposited in each anions, with the third and fifth peak potentials corresponding to 2e− transfer processes are present in the CV of PMo12O402−. In contrast, only five redox peaks are observed for HPMo12O40 with the third and fifth peaks corresponding to 2e− transfer processes. The peak potentials of the two charge states of POM are in agreement with values reported previously for [PMo12O40]2− (25), which validates the accuracy of cell 1. The formal redox potentials (E0) of peaks 1−5 of PMo12O40−2 and HPMo12O40−2 calculated by the average of Epeak and Eredox indicate no changes associated with the energy barriers for each redox step as a function of the POM charge state. The number of electrons transferred in the first four redox steps is similar for both PMo12O40−2 and HPMo12O40−2. A clear deviation in the mechanism of electron transfer processes for the two charge states is observed starting only from the fifth redox peak. The [PMo12O40]2− ions undergo 2e−/2H+ transfer in protic and 1e− transfer in aprotic electrolytes (25). The presence of trace amounts of protons resulting from deprotonation of HPMo12O40−2 in the electrolyte or on the electrode surface may be responsible for the earlier onset of the 2e− processes observed for the 2− charge state of POM. Furthermore, distinct differences are observed in the current functions (Rox and Rred) listed in Table 1. Higher values of Rox in comparison with Rred are attributed to differences in the oxidation and reduction parts of the EDL formed by asymmetric electrolyte ions (EMIM+ and BF4−) (26). The Rox of the first two redox peaks (1, 2) are similar for both charge states. However, a significant decrease in Rox is observed for HPMo12O40−2 in comparison with PMo12O40−2 for peaks 3−5. The decrease is attributed to the presence of H+ ions in HPMo12O40−2 that may inhibit electron transfer to POM. These results demonstrate the exceptional micrographs (Fig. 1C), which ensures a surplus amount of electrolyte ions in the bulk diffusion region. These results indicate that ions deposited on the top surface of the IL membrane readily diffuse to the underlying electrode much like in liquid cells. Similarly, the diffusion coefficient of ions of (7.9 ± 1.9) × 10−7 cm2/s and the Nernst diffusion layer thickness of ∼2.6 μm are calculated using the EIS data for cell 2 with IL in vacuum (SI Appendix, Fig. S3 B, 2 and Eqs. S2–54). The diffusion coefficient is of the same order of magnitude as the value determined for typical proton-conducting membranes used in PEMFCs (e.g., 5 × 10−7 cm2/s for Nafion) (24). An increase in diffusion layer thickness is attributed to increased ionic diffusion due to higher occupancy of smaller H+ ions at the electrode surface and the smaller surface area of the ITO compared with Pt working electrode (WE). For cell 2 with Nafion, the diffusion coefficient and Nernst diffusion layer thickness are estimated to be 2.5 × 10−8 cm2/s and 24 nm, respectively (SI Appendix, Fig. S3 B, 2). The diffusion coefficient of the Nafion is smaller than the literature values, which is attributed to the lower thickness of Nafion used in this study.

In Situ Redox Electrochemistry of POM Anions. Redox properties of both intact POM anions present in solution (PMo12O40−2 and HPMo12O40−2) and POM fragments (Mo7O22−2 and PMo3O19−2) generated by gas-phase CID that cannot be produced in solution are soft-landed at a kinetic energy of 30 eV per charge (SI Appendix, Figs. S4–S6) and examined using cell 1. CV of the soft-landed anions is performed in vacuum after deposition of ~1 × 1014 ions on cell 1. Typical CVs of PMo12O40−2 and HPMo12O40−2 anions at a scan rate of 10 mV s−1 are shown in Fig. 3 A. CVs acquired at different scan rates are shown in SI Appendix, Figs. S7 and S8. The CV curves were shifted manually during data processing to maintain the reduction potential of Ce/Ce+ at the value of −1,520 mV observed before SL. The CVs acquired at different scan rates demonstrate that all of the peaks follow typical Randles–Sevčik behavior. The estimated electrochemical parameters including oxidation and reduction peak potentials (Epeak and Ered), current functions (Rox and Rred), current function is the ratio of the peak current to the square root of the scan rate), and the number of electrons transferred (n) for the first five and for all redox peaks of PMo12O40−2 and HPMo12O40−2 are summarized in Table 1 and SI Appendix, Table S2, respectively.

Eight reversible redox couples in which the third and sixth peaks correspond to 2e− while the other peaks correspond to 1e− transfer processes are present in the CV of PMo12O40−2. In contrast, only five redox peaks are observed for HPMo12O40−2 with the third and fifth peaks corresponding to 2e− transfer processes. The peak potentials of the two charge states of POM are in agreement with values reported previously for [PMo12O40]2− (25), which validates the accuracy of cell 1. The formal redox potentials (E0) of peaks 1−5 of PMo12O40−2 and HPMo12O40−2 calculated by the average of Epeak and Eredox indicate no changes associated with the energy barriers for each redox step as a function of the POM charge state. The number of electrons transferred in the first four redox steps is similar for both PMo12O40−2 and HPMo12O40−2. A clear deviation in the mechanism of electron transfer processes for the two charge states is observed starting only from the fifth redox peak. The [PMo12O40]2− ions undergo 2e−/2H+ transfer in protic and 1e− transfer in aprotic electrolytes (25). The presence of trace amounts of protons resulting from deprotonation of HPMo12O40−2 in the electrolyte or on the electrode surface may be responsible for the earlier onset of the 2e− processes observed for the 2− charge state of POM. Furthermore, distinct differences are observed in the current functions (Rox and Rred) listed in Table 1. Higher values of Rox in comparison with Rred are attributed to differences in the oxidation and reduction parts of the EDL formed by asymmetric electrolyte ions (EMIM+ and BF4−) (26). The Rox of the first two redox peaks (1, 2) are similar for both charge states. However, a significant decrease in Rox is observed for HPMo12O40−2 in comparison with PMo12O40−2 for peaks 3−5. The decrease is attributed to the presence of H+ ions in HPMo12O40−2 that may inhibit electron transfer to POM. These results demonstrate the exceptional...
Table 1. Estimated electrochemical parameters including oxidation (E_{p,ox}) and reduction (E_{p,red}) peak potentials, oxidation (R_{ox}) and reduction (R_{red}) current functions, and the number of electrons (n) transferred for the first five peaks observed for PMo_{12}O_{40}^{6-}, HPMo_{12}O_{46}^{6-}, MoO_{27}^{7-}, and PMo_{10}O_{48}^{8-} measured using cell 1

<table>
<thead>
<tr>
<th>Peak no.</th>
<th>E_{p,ox}/E_{p,red} (mV)</th>
<th>R_{ox}/R_{red}</th>
<th>E_{p,ox}/E_{p,red} (mV)</th>
<th>R_{ox}/R_{red}</th>
<th>E_{p,ox}/E_{p,red} (mV)</th>
<th>R_{ox}/R_{red}</th>
<th>E_{p,ox}/E_{p,red} (mV)</th>
<th>R_{ox}/R_{red}</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>-64/-90</td>
<td>234/120</td>
<td>1</td>
<td>-67/-90</td>
<td>244/67</td>
<td>1</td>
<td>0</td>
<td>-61/404</td>
</tr>
<tr>
<td>2</td>
<td>-350/-380</td>
<td>226/152</td>
<td>1</td>
<td>-353/-385</td>
<td>239/88</td>
<td>1</td>
<td>-351/-419</td>
<td>45/8</td>
</tr>
<tr>
<td>3</td>
<td>-765/-81</td>
<td>152/40</td>
<td>2</td>
<td>-717/-740</td>
<td>82/43</td>
<td>2</td>
<td>-529/-507</td>
<td>5/25</td>
</tr>
<tr>
<td>4</td>
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<td>203/132</td>
<td>1</td>
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<td>1</td>
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<td>2/2</td>
</tr>
<tr>
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<td>14/28</td>
<td>2</td>
<td>-777/-790</td>
<td>4/4</td>
</tr>
</tbody>
</table>

Current function, R_{ox} = (i_{p,ox}/ν^1/2)/10^{-4} and R_{red} = (i_{p,red}/ν^1/2)/10^{-4}, where i_{p,ox} and i_{p,red} are oxidation and reduction peak currents, respectively (A), ν = scan rate (V/s).

capability of cell 1 combined with ion SL to explore the charge-state dependence of the redox pathways of complex ions at EEs, something that is not possible with other techniques.

Redox properties of complementary building blocks of [PMo_{12}O_{40}^{6-}] that contribute to the overall multielectron redox activity of the intact cluster are also examined in this study. The electronic properties of [PMo_{12}O_{40}^{6-}] in the gas phase have been extensively studied (27, 28), in which the intramolecular charge transfer is critical for efficient participation of all Mo atoms of the [PMo_{12}O_{40}^{6-}] cluster in multielectron redox processes at EEs that have not been explored. CID combined with SL is ideally suited for studying the structures and reactivity of ionic species that cannot be prepared in solution (29, 30). Previously, a substantial difference was observed in the chemical reactivity of SL ruthenium tris(bipyridine) dication, Ru(bpy)_3^2+ and [bpy = Tris(bipyridine) ligand] and their undercoordinated analog, Ru(bpy)_3^3+, producing insoluble CID (29). Similar observations were also made for fully and partially phosphine-ligated gold cluster cations generated by CID (30). In this study, mass-selected MoO_{27}^{7-} and PMo_{10}O_{48}^{8-} fragments, generated by CID, are deposited onto different in situ cells (cell 1) and their redox activity is characterized using CV.

The CVs of both MoO_{27}^{7-} (Fig. 3B) and PMo_{10}O_{48}^{8-} (Fig. 3C) show a combination of reversible and irreversible oxidation and reduction peaks. The CV of MoO_{27}^{7-} shows 10 oxidation peaks and 8 reduction peaks, whereas the CV of PMo_{10}O_{48}^{8-} contains 2 oxidation peaks and 5 reduction peaks. All of the peaks follow Randles–Sevcik behavior (SI Appendix, Figs. S9 and S10). The number of redox peaks observed for MoO_{27}^{7-} matches the number of peaks observed for PMo_{12}O_{40}^{6-} within the same potential range (Fig. 3A and B). Similar peak potentials are observed for the first three reversible peaks of PMo_{12}O_{40}^{6-} and MoO_{27}^{7-} (Table 1). The first oxidation and reduction peaks (peak 1) of PMo_{12}O_{40}^{6-} are shifted by 60 and 30 mV, respectively, toward lower values in comparison with MoO_{27}^{7-} and the calculated R_{ox} of the first peak is substantially lower than the value obtained for MoO_{27}^{7-}. These findings indicate that electron transfer in the first redox couple is more efficient for MoO_{27}^{7-} compared with PMo_{12}O_{40}^{6-}. In contrast, substantially lower R_{ox} and R_{red} values are observed for all other redox peaks of MoO_{27}^{7-} in comparison with PMo_{12}O_{40}^{6-} (Table 1 and SI Appendix, Table S5). This observation indicates inefficient electron transfer from the MoO_{27}^{7-} cluster to the electrode in all subsequent redox steps.

In contrast, the CV of the PMo_{10}O_{48}^{8-} fragment is characterized by broad oxidation and reduction peaks with significantly higher values of R_{ox} and R_{red} over the entire potential range (Fig. 3C and Table 1). The difference in the width and intensity of the oxidation and reduction peaks of MoO_{27}^{7-} and PMo_{10}O_{48}^{8-} may be attributed either to changes in adsorption of these ions on the electrode surface due to variations in their effective dipole moments or the presence of overlapping peaks corresponding to multiple isomers with distinct electronic properties as described in previous computational studies (31). The presence of narrow redox peaks in the CVs for both fragments rules out the possibility of dissimilar adsorption on the WE, which would influence each of the peaks systematically. Therefore, it is most likely that the broad first reduction and oxidation peaks observed for PMo_{10}O_{48}^{8-} originate from the presence of multiple isomers with substantially different overpotentials that contribute to several overlapping redox peaks in the CV. Furthermore, except for peak 1 of MoO_{27}^{7-}, substantially higher values of R_{ox} and R_{red} are observed for all the rest of the peaks for PMo_{10}O_{48}^{8-} in comparison with MoO_{27}^{7-} (Table 1). In the case of Keggin PMo_{12}O_{40}^{6-}, where these two fragments are assembled together, higher R_{ox} and R_{red} values are observed for all redox peaks.

The CV results may be rationalized by assuming that redox properties of PMo_{12}O_{40}^{6-} are affected by the synergistic interaction between the two building blocks, MoO_{27}^{7-} and PMo_{10}O_{48}^{8-}, and electron transfer within the cluster. These observations provide information about the contribution of individual building blocks of metal oxide clusters to the overall redox activity. To confirm that the PMO anions are deposited intact on the cell surface, identical SL experiments were conducted at a lower kinetic energy of 5 eV per charge. Similar CVs were obtained for the soft-landed POM anions at two different kinetic energies (SI Appendix, Fig. S11), indicating that POM anions do not undergo dissociation upon landing on the cell surface. Collectively, these results demonstrate that SL combined with the in situ cell developed in this study constitutes a powerful tool for characterizing the intrinsic redox properties of complex redox-active species at well-defined EEs, including species that cannot be prepared in solution.

**Reactive Electrochemistry on Bare Pt Clusters.** The ORR activity (catalytic process) on well-defined soft-landed bare Pt clusters (~Pt_{10}) is evaluated using protic IL to demonstrate the ability of the thin-film electrochemical cell to mimic the acidic electrolyte environment relevant to traditional catalytic studies in aqueous solution. A comparative ORR experiment was also performed using cell 2 with Nafion. Of note is that ORR on Pt follows a four-electron pathway in both protic IL and aqueous acidic electrolyte (e.g., Nafion) (32) and the intrinsic ORR activity should not change between protic IL and Nafion electrolyte. Approximately 2 × 10^{12} bare anionic Pt clusters produced by magnetron sputtering and gas aggregation (33, 34) are uniformly deposited onto both variants of cell 2 and characterized by CV under a N_{2} or O_{2} atmosphere (Fig. 4). The CVs of pristine cell 2 with IL (Fig. 4) and Nafion (SI Appendix, Fig. S12) under N_{2} show characteristic non-Faradaic behavior in the potential range where ORR is known to occur, which confirms the stability of the cell. In comparison, in an O_{2} atmosphere, pristine cell 2 with IL reveals the presence of the ORR at an onset potential of ~750 mV and the ORR current measured at ~1,000 mV was ~3.7 μA. No
significant ORR current was observed in pristine cell 2 with Nafion in the presence of O2. In contrast, the CV of cell 2 with IL membrane containing soft-landed Pt clusters acquired in a N2 atmosphere shows the characteristic H+ adsorption and desorption regions arising from the presence of protons in the fully dehydrated proton-conducting IL membrane. The H+ adsorption and desorption regions do not exhibit well-defined peaks corresponding to specific Pt facets because small (~1 nm) Pt clusters do not contain such well-defined facets like larger NPs (35). The calculated electrochemically active surface area (ECSA) of 38 m2/gPt using SI Appendix, Eq. SS is comparable to values reported previously for Pt-based catalysts (36), indicating that most of the deposited Pt clusters reach the electrode surface after SL. Cell 2 with Nafion in the presence of bare Pt clusters and humidified N2 shows significant reduction current below 0 V, which is attributed either to H+ adsorption and desorption or H2 evolution. Due to this uncertainty, the ECSA was not estimated in this case. For cell 2 with IL, Pt clusters in an O2 atmosphere show well-resolved ORR curves characterized by an increase of 60 μA reduction current at ~1,000 mV with an onset potential of ~300 mV, which is 450 mV higher than the onset of ORR on pristine cell 2 without clusters. The area-specific and mass-specific activity was estimated to be 677 μA/cm2 and 0.26 A/mgPt, respectively. The decrease of 100 mV in the onset potential and higher specific activities observed for Pt clusters in comparison with literature values (37) is attributed to the superior ORR activity of the soft-landed species. It follows that the proton-conducting IL membrane used in this study facilitates diffusion of O2 to the electrode surface and provides sufficient amounts of protons to promote the ORR. For comparison, significant ORR activity was observed for cell 2 with Nafion on bare Pt clusters with the onset potential of 500 mV and reduction current of 23 μA (SI Appendix, Fig. S12B). A significant Pt oxide formation at ~510 mV was observed typical of the ORR occurring in aqueous acidic electrolyte. The observed onset potential of the ORR is lower than the values reported for ORR in Nafion, indicating the lower ORR activity of Pt clusters in this cell (36). This could be attributed to either an increase in interfacial resistance due to immobilization or agglomeration of bare Pt clusters on the electrode interface, both of which may result in an increase in the overpotential. The ability to study reactive electrochemistry using cell 2 opens up opportunities for examining the catalytic activity of well-defined bare clusters and NPs that cannot be generated using traditional synthesis approaches.

In summary, the in situ thin-film electrochemical cells reported in this study are ideally suited for characterizing redox and reactive processes at well-defined EEIs. The thin-film cells are compatible with various state-of-the-art deposition techniques and demonstrate excellent stability in diverse controlled environments ranging from high vacuum to atmospheric pressure. Furthermore, cells 1 and 2 exhibit comparable mass-transfer properties at the EEI as evidenced by their estimated diffusion coefficients, in comparison with liquid electrochemical cells and commercial PEMFC electrolytes, respectively. These results indicate that much like in liquid electrochemical cells, ions deposited onto the surface of the solid IL membranes readily diffuse to the WE to participate in redox processes. Several examples presented in this study demonstrate the potential of the in situ cells combined with SL and in-source CID for studying redox properties of novel states of both intact ions and their fragments. This provides detailed insights into the contribution of different building blocks to the overall redox activity of clusters that cannot be studied experimentally using existing approaches. In addition, in situ proton-conducting IL cells may be used for examining the electrocatalytic activity of bare metal clusters formed in the gas phase that are not accessible using synthesis in solution. The approach offers a platform to study critical electrochemical processes taking place in functional devices and thus acquire an in-depth understanding of electrode kinetics which may lead to rational design of efficient, sustainable, and high-performance EEI for solid-state electrochemical systems with applications in catalysis as well as energy conversion and storage.

Materials and Methods

Fabrication of in Situ IL Thin-Film Electrochemical Cells. Two types of in situ IL cells were fabricated on commercially available Pt and ITO SPE electrodes (Dropsens, Spain) for studying redox and reactive electrochemistry, respectively. Cell 1 containing a nonaqueous aprotic IL membrane on Pt SPE was used for studying the intrinsic redox activity of soft-landed ions, whereas cells containing a nonaqueous proton-conducting IL membrane (cell 2) on ITO SPE were used for examining the electrocatalytic activity of bare Pt clusters toward the ORR. Another variant of cell 2 was prepared with a thin Nafion membrane instead of IL membrane to represent the conventional PEMFC interface. The Pt SPE consists of a Pt working electrode (WE), Pt counter electrode (CE), and Ag reference electrode (RE) as shown in Fig. 1A. The ITO SPE consists of an ITO-coated WE, carbon CE, and Ag RE. The approximate geometric area of the WE for both Pt and ITO SPEs is 7 × 10−6 m2. Further details describing the preparation of in situ cells are provided in the SI Appendix. The cell holder is equipped with a three-pin connector wired to an electrical vacuum feedthrough providing electrical connections from the WE, CE, and RE to a potentiostat (Versastart 3, Princeton Applied Research).

Morphology of the IL Membrane of the in Situ Cell. The surface morphology and thickness of the IL membrane of cell 1 was examined using high-resolution electron microscopy (SEM) (Quanta 3D model, FEI, Inc.) operated at 10-kV acceleration voltage. The fabricated in situ cell was cut with a razor blade and the cross-section of the IL membrane on top of the WE was examined. Similarly, the layer of IL membrane was peeled off to examine its interior.

SL of Redox-Active Cluster Ions and Bare Pt Cluster Ions. Two SL instruments described in more detail in the SI Appendix were used in this study. In the first instrument, shown in SI Appendix, Fig. S4 (38, 39), ions are produced using electrospray ionization (ESI) of Na[PMO12O40] in H2O in methanol and transferred into the vacuum system using a heated stainless steel inlet where they undergo desolvation. Ions are subsequently transferred using a dual ion funnel system, mass-selected using a quadrupole mass filter, and deposited onto the electrochemical cell at a kinetic energy of 30–35 eV per charge. Additional experiments were performed with lower kinetic energy of 5 eV per charge to confirm that POM anions are deposited intact on the cell surface. The total number of ions deposited was calculated by integrating the ion current over time. A typical ESI mass spectrum of a Na[PMO12O40] solution (SI Appendix, Fig. S5) contains stable PMO12O40 and HPMO12O40 anions at m/z = 608 and 911, respectively (40, 41), both of which were examined in this study. In addition, the two most abundant complementary fragment ions, Mo6O162− (m/z = 512) and PMo12O40 (m/z = 788), produced by in-source CID of PMO12O40 (SI Appendix, Fig. S6) were mass-selected and deposited onto the in situ IL cell. In CID, molecular ions are accelerated by electric fields and fragment ions are generated through energetic collisions.
of precursor ions with neutral gas molecules. In this study, in-source CID was achieved by increasing the rf of both ion funnels and adjusting the potential difference between the end plate of the second ion funnel and the dc offset of the collisional quadrupole. In the second instrument, SL of bare anionic Pt clusters was achieved using the modified commercial Nanogen-Trio cluster source and Q-Prep 500 deposition system (Mantis Deposition Ltd.) (33, 34). The bare anionic Pt clusters were produced by dc magnetron sputtering of a circular Pt target in a controlled flow of ultra-high-purity argon and helium and deposited onto cell 2 without mass selection. The peak of the anionic Pt cluster distribution was maintained at ~6,000 amu corresponding to ~$^{2+}$ and a cluster size of ~1 nm.

**Electrochemical Experiments.** CV and EIS were used to study the characteristics of the in situ IL cells (cells 1 and 2). CV was used to determine the redox electrochemistry of SL POM anions using cell 1 and ORR activity (reactive electrochemistry) of bare Pt clusters using two variants of cell 2, respectively. Further details describing the electrochemical experiments performed using cells 1 and 2 are provided in the SI Appendix. All CV and EIS experiments presented in this study were repeated at least five times.

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