

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

Venkateshkumar Prabhakaran^a, Grant E. Johnson^a, Bingbing Wang^{b,1}, and Julia Laskin^{a,2}

^aPhysical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352; and ^bEnvironmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352

Edited by R. Graham Cooks, Purdue University, West Lafayette, IN, and approved October 10, 2016 (received for review May 31, 2016)

Molecular-level understanding of electrochemical processes occurring at electrode–electrolyte interfaces (EEl) 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 EEl 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 EEl. Using an aprotic cell, the effect of charge state ($\text{PMo}_{12}\text{O}_{40}^{3-/2-}$) and the contribution of building blocks of Keggin polyoxometalate (POM) clusters to redox processes are characterized by populating EEl 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 (Pt_{30} ~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 EEl in solid-state redox systems and reactive electrochemistry at precisely defined conditions. This capability will advance the molecular-level understanding of processes occurring at EEl that are critical to many energy-related technologies.

in situ electrochemistry | electrode–electrolyte interface | ion soft-landing | ionic liquid membrane | clusters

Understanding the intrinsic properties of electroactive species on electrode surfaces is critical to the rational design of stable and efficient electrode–electrolyte interfaces (EEl) 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 EEl (3). Agglomeration and decomposition of redox-active species in supercapacitors, evolution of resistive lithium metal dendrites at the solid–electrolyte interphase 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 EEl 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 EEl 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 EEl 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 EEl (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 EEl, the majority of in situ approaches rely on specially designed liquid electrochemical cells. New approaches for studying solid EEl, 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 EEl 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 EEl precisely designed using soft-landing (SL) of mass- and charge-selected ions (6–12). Previously, the superior performance of EEl prepared using SL in comparison with drop casting and electrospray deposition was demonstrated (13). The high specific capacitance and improved stability of EEl 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 EEl prepared using traditional techniques including direct painting, ambient air spray, and electrodeposition (3). Elimination of strongly coordinating counterions and solvent molecules that alter the distribution and stoichiometry of the compounds of interest at EEl facilitates characterization of the intrinsic activity of precisely defined species.

Significance

In situ characterization of kinetics at electrode–electrolyte interfaces (EEl) 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 EEl 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 EEl generated using ion soft-landing (SL) in controlled environments, both in vacuum and in the presence of reactant gases. Populating EEl 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 EEl during operation.

Author contributions: V.P., G.E.J., and J.L. designed research; V.P. and G.E.J. performed research; V.P., G.E.J., and B.W. contributed new reagents/analytic tools; V.P., G.E.J., and J.L. analyzed data; and V.P., G.E.J., and J.L. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

¹Present address: State Key Laboratory of Marine and Environmental Science and College of Ocean and Earth Sciences, Xiamen University, Xiamen 361102, China.

²To whom correspondence should be addressed. Email: Julia.Laskin@pnnl.gov.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1608730113/-DCSupplemental.

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 solid 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 POM 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 (Cc/Cc⁺) 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 electric 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 (Cc/Cc⁺) with the formal potential at ~1,480 mV (Fig. 2 and *SI Appendix*, Fig. S2); (iii) efficient diffusion of ions [diffusion coefficient of $(4.9 \pm 2.1) \times 10^{-7}$ cm²/s for Cc/Cc⁺ in EMIMBF₄] in the IL membrane as determined by CV of Cc/Cc⁺ at different scan rates (*SI Appendix*, Fig. S2 and Table S1) using the Randles-Sevcik equation (*SI Appendix*, Eq. S1). The value of the diffusion coefficient is of the same order of magnitude as values reported in the literature ($\sim 1.1 \times 10^{-7}$ cm²/s) for Cc/Cc⁺ 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 $\sim (6.0 \pm 3.2) \times 10^{-7}$ 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

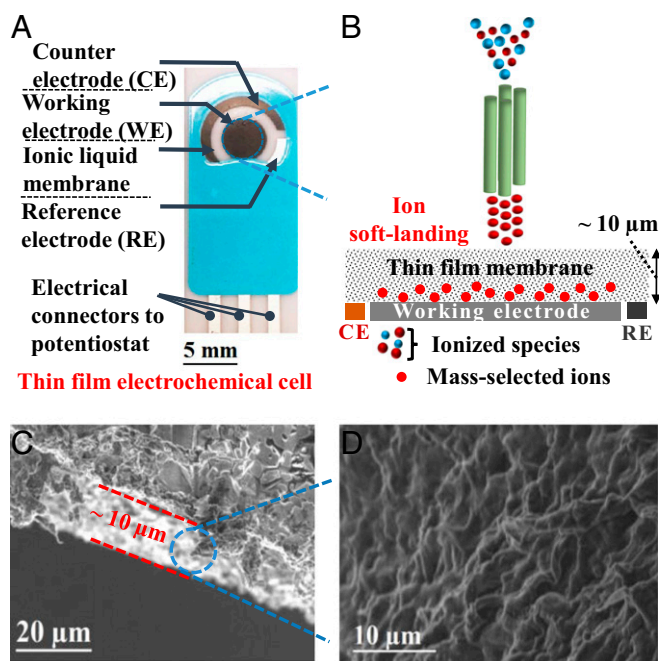


Fig. 1. (A) Image of the three-electrode solid-state in situ IL electrochemical cell for performing redox and reactive electrochemistry. (B) Schematic representation of a well-defined EEI prepared using SL. (C and D) Scanning electron micrographs of the cross-section and interior of the IL membrane present in the in situ IL cell, respectively.

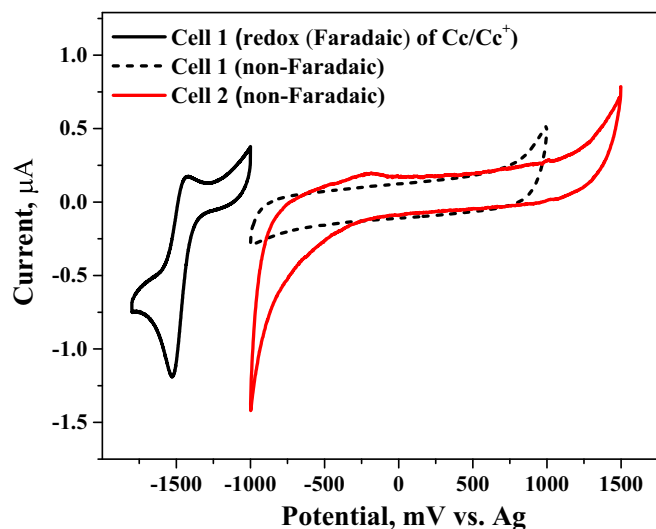


Fig. 2. CVs of the (i) aprotic in situ cell (cell 1) acquired in two potential ranges in vacuum to represent the redox (Faradaic) behavior of the Cc/Cc^+ IRRC observed between $-1,800$ and $-1,000$ mV vs. Ag, and a typical EDL (non-Faradaic) behavior observed between $-1,000$ and $1,000$ mV vs. Ag; scan rate, 10 mV s^{-1} and (ii) protic in situ IL cell (cell 2) acquired in vacuum to present the non-Faradaic behavior observed between $-1,000$ and $1,500$ mV vs. Ag; scan rate, 10 mV s^{-1} .

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 $(7.9 \pm 1.9) \times 10^{-7} \text{ cm}^2/\text{s}$ and the Nernst diffusion layer thickness of $\sim 2.6 \mu\text{m}$ are calculated using the EIS data for cell 2 with IL in vacuum (SI Appendix, Fig. S3 B, 2 and Eqs. S2–S4). The diffusion coefficient is of the same order of magnitude as the value determined for typical proton-conducting membranes used in PEMFCs (e.g., $\sim 5 \times 10^{-7} \text{ cm}^2/\text{s}$ 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 $2.5 \times 10^{-8} \text{ cm}^2/\text{s}$ 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 ($PMo_{12}O_{40}^{3-}$ and $HPMo_{12}O_{40}^{2-}$) and POM fragments ($Mo_7O_{22}^{2-}$ and $PMo_5O_{18}^{-}$) 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 $\sim 1 \times 10^{14}$ ions on cell 1. Typical CVs of $PMo_{12}O_{40}^{3-}$ and $HPMo_{12}O_{40}^{2-}$ anions at a scan rate of 10 mV s^{-1} are shown in Fig. 3A. 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 Cc/Cc^+ at the value of $-1,520 \text{ mV}$ observed before SL. The CVs acquired at different scan rates demonstrate that all of the peaks follow typical Randles-Sevcik behavior. The estimated electrochemical parameters including oxidation and reduction peak potentials ($E_{p,ox}$ and $E_{p,red}$), current functions (R_{ox} and R_{red}) (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

$PMo_{12}O_{40}^{3-}$ and $HPMo_{12}O_{40}^{2-}$ 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 $PMo_{12}O_{40}^{3-}$. In contrast, only five redox peaks are observed for $HPMo_{12}O_{40}^{2-}$ 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 $[PMo_{12}O_{40}]$ (25), which validates the accuracy of cell 1. The formal redox potentials (E_f) of peaks 1–5 of $PMo_{12}O_{40}^{3-}$ and $HPMo_{12}O_{40}^{2-}$ calculated by the average of $E_{p,ox}$ and $E_{p,red}$ 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 $PMo_{12}O_{40}^{3-}$ and $HPMo_{12}O_{40}^{2-}$. 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 $[PMo_{12}O_{40}]$ anions undergo $2e^-/2H^+$ transfer in protic and $1e^-$ transfer in aprotic electrolytes (25). The presence of trace amounts of protons resulting from deprotonation of $HPMo_{12}O_{40}^{2-}$ 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 (R_{ox} and R_{red}) listed in Table 1. Higher values of R_{ox} in comparison with R_{red} are attributed to differences in the oxidation and reduction parts of the EDL formed by asymmetric electrolyte ions ($EMIM^+$ and BF_4^-) (26). The R_{ox} of the first two redox peaks (1, 2) are similar for both charge states. However, a significant decrease in R_{ox} is observed for $HPMo_{12}O_{40}^{2-}$ in comparison with $PMo_{12}O_{40}^{3-}$ for peaks 3–5. The decrease is attributed to the presence of H^+ ions in $HPMo_{12}O_{40}^{2-}$ that may inhibit electron transfer to POM. These results demonstrate the exceptional

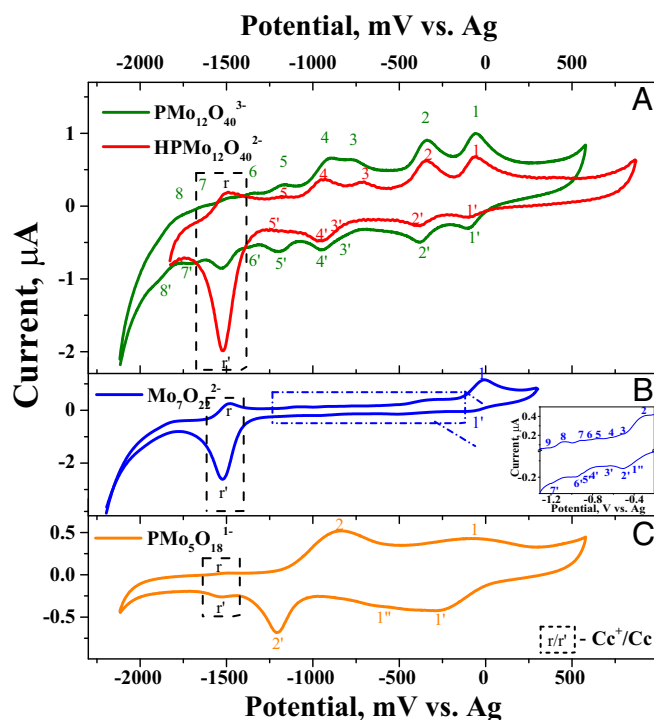


Fig. 3. CVs of cell 1 with soft-landed (A) $PMo_{12}O_{40}^{3-}$ and $HPMo_{12}O_{40}^{2-}$ anions, and major fragments of $PMo_{12}O_{40}^{3-}$, (B) $Mo_7O_{22}^{2-}$, and (C) $PMo_5O_{18}^{-}$. (B, Inset) Enlarged region between $-1,300$ and -200 mV . All CVs were performed at a scan rate of 10 mV s^{-1} . Approximately 1×10^{14} ions were deposited in each case. Dashed black rectangles highlight oxidation (r) and reduction (r') peaks of the Cc/Cc^+ IRRC.

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 $PMo_{12}O_{40}^{3-}$, $HMo_{12}O_{40}^{2-}$, $Mo_7O_{22}^{2-}$, and $PMo_5O_{18}^{-}$ measured using cell 1

Peak no.	$PMo_{12}O_{40}^{3-}$			$HMo_{12}O_{40}^{2-}$			$Mo_7O_{22}^{2-}$				$PMo_5O_{18}^{-}$			
	$E_{p,ox}/E_{p,red}$	R_{ox}/R_{red}	n	$E_{p,ox}/E_{p,red}$	R_{ox}/R_{red}	n	$E_{p,ox}$	$E_{p,red}$	R_{ox}	R_{red}	$E_{p,ox}$	$E_{p,red}$	R_{ox}	R_{red}
	mV	$A/(V/s)^{-0.5}$		mV	$A/(V/s)^{-0.5}$		mV	$A/(V/s)^{-0.5}$			mV	$A/(V/s)^{-0.5}$		
1	-64/-90	234/120	1	-67/-90	244/67	1	0	-61	404	89	-46	-233	66	164
2	-350/-380	226/152	1	-353/-385	239/88	1	-351	-419	45	8	-877	-450	175	16
3	-765/-810	152/40	2	-717/-740	82/43	2	-529	-507	5	25	—	-659	—	7
4	-921/-950	203/132	1	-960/-950	139/132	1	-641	-670	2	2	—	-860	—	288
5	-1,170/-1,173	51/71	1	-1,184/-1,165	14/28	2	-777	-790	4	4	—	-1,197	—	21

Current function, $R_{ox} = (i_{p,ox}/\nu)/10^{-8}$ and $R_{red} = (i_{p,red}/\nu)/10^{-8}$, 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 EEIs, something that is not possible with other techniques.

Redox properties of complementary building blocks of $[PMo_{12}O_{40}]$ that contribute to the overall multielectron redox activity of the intact cluster are also examined in this study. The electronic properties of $[PMo_{12}O_{40}]$ in the gas phase have been extensively studied (27, 28), but intramolecular charge transfer which is critical for efficient participation of all Mo atoms of the $[PMo_{12}O_{40}]$ cluster in multielectron redox processes at EEIs has 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 trisbipyridine dications, $Ru(bpy)_3^{2+}$, [$bpy = Tris(bipyridine)$ ligand] and their undercoordinated analog, $Ru(bpy)_2^{2+}$, produced using in-source 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 $Mo_7O_{22}^{2-}$ and $PMo_5O_{18}^{-}$ 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 $Mo_7O_{22}^{2-}$ (Fig. 3B) and $PMo_5O_{18}^{-}$ (Fig. 3C) show a combination of reversible and irreversible oxidation and reduction peaks. The CV of $Mo_7O_{22}^{2-}$ shows 10 oxidation peaks and 8 reduction peaks, whereas the CV of $PMo_5O_{18}^{-}$ 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 $Mo_7O_{22}^{2-}$ matches the number of peaks observed for $PMo_{12}O_{40}^{3-}$ within the same potential range (Fig. 3A and B). Similar peak potentials are observed for the first three reversible peaks of $PMo_{12}O_{40}^{3-}$ and $Mo_7O_{22}^{2-}$ (Table 1). The first oxidation and reduction peaks (peak 1) of $PMo_{12}O_{40}^{3-}$ are shifted by 60 and 30 mV, respectively, toward lower values in comparison with $Mo_7O_{22}^{2-}$, and the calculated R_{ox} of the first peak is substantially lower than the value obtained for $Mo_7O_{22}^{2-}$. These findings indicate that electron transfer in the first redox couple is more efficient for $Mo_7O_{22}^{2-}$ compared with $PMo_{12}O_{40}^{3-}$. In contrast, substantially lower R_{ox} and R_{red} values are observed for all other redox peaks of $Mo_7O_{22}^{2-}$ in comparison with $PMo_{12}O_{40}^{3-}$ (Table 1 and SI Appendix, Table S3). This observation indicates inefficient electron transfer from the $Mo_7O_{22}^{2-}$ cluster to the electrode in all subsequent redox steps.

In contrast, the CV of the $PMo_5O_{18}^{-}$ 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 $Mo_7O_{22}^{2-}$ and $PMo_5O_{18}^{-}$ 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 $PMo_5O_{18}^{-}$ 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 $Mo_7O_{22}^{2-}$, substantially higher values of R_{ox} and R_{red} are observed for all the rest of the peaks for $PMo_5O_{18}^{-}$ in comparison with $Mo_7O_{22}^{2-}$ (Table 1). In the case of Keggin $PMo_{12}O_{40}^{3-}$, 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 $PMo_{12}O_{40}^{3-}$ are affected by the synergistic interaction between the two building blocks, $Mo_7O_{22}^{2-}$ and $PMo_5O_{18}^{-}$, 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 POM 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 the 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 EEIs, 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 ($\sim Pt_{30}$) 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. S12A) 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

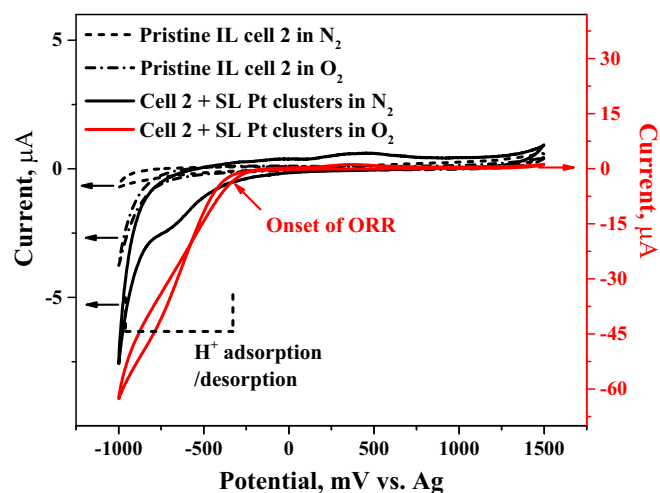


Fig. 4. CVs of pristine cell 2 with IL, and IL cell 2 containing 2×10^{12} soft-landed bare Pt clusters acquired under N_2 and O_2 atmosphere. ORR activity is observed for both pristine cell and cell containing soft-landed Pt clusters in O_2 . Scan rate, 50 mV s^{-1} .

significant ORR current was observed in pristine cell 2 with Nafion in the presence of O_2 . In contrast, the CV of cell 2 with IL membrane containing soft-landed Pt clusters acquired in a N_2 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 ($\sim 1 \text{ nm}$) Pt clusters do not contain such well-defined facets like larger NPs (35). The calculated electrochemically active surface area (ECSA) of $38 \text{ m}^2/\text{g}_{\text{Pt}}$ using *SI Appendix, Eq. S5* 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 N_2 shows significant reduction current below 0 V, which is attributed either to H^+ adsorption and desorption or H_2 evolution. Due to this uncertainty, the ECSA is not estimated in this case. For cell 2 with IL, Pt clusters in an O_2 atmosphere show well-resolved ORR curves characterized by an increase of $60 \mu\text{A}$ reduction current at $-1,000 \text{ mV}$ 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 $677 \mu\text{A}/\text{cm}^2$ and $0.26 \text{ A}/\text{mg}_{\text{Pt}}$, 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 O_2 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 $23 \mu\text{A}$ (*SI Appendix, Fig. S12B*). A significant Pt oxide formation at $\sim 510 \text{ mV}$ 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 counterelectrode (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 $7 \times 10^{-6} \text{ m}^2$. 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 (Versastat 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 a scanning 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 $\text{Na}_3[\text{PMo}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$ 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 $30\text{--}35 \text{ eV}$ 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 $\text{Na}_3[\text{PMo}_{12}\text{O}_{40}]$ solution (*SI Appendix, Fig. S5*) contains stable $\text{PMo}_{12}\text{O}_{40}^{3-}$ and $\text{HPMo}_{12}\text{O}_{40}^{2-}$ 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, $\text{Mo}_7\text{O}_{22}^{2-}$ ($m/z = 512$) and $\text{PMo}_5\text{O}_{18}^{3-}$ ($m/z = 798$), produced by in-source CID of $\text{PMo}_{12}\text{O}_{40}^{3-}$ (*SI Appendix, Fig. S6*) (40) 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 ~Pt₃₀ 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.

ACKNOWLEDGMENTS. This work was supported by the US Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division. The research was performed using Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PNNL). PNNL is operated by Battelle for DOE under Contract DE-AC05-76RL01830.

1. Bard AJ, et al. (1993) The electrode/electrolyte interface - a status report. *J Phys Chem* 97(28):7147-7173.
2. Srinivasan S (2006) Electrode/electrolyte interfaces: Structure and kinetics of charge transfer. *Fuel Cells: From Fundamentals to Applications*, ed Srinivasan S (Springer US, Boston), pp 27-92.
3. Shen PK, Wang C-Y, Jiang SP, Sun X, Zhang J (2015) *Electrochemical Energy: Advanced Materials and Technologies* (CRC Press, Boca Raton, FL), pp 1-170.
4. Forse AC, Merlet C, Griffin JM, Grey CP (2016) New perspectives on the charging mechanisms of supercapacitors. *J Am Chem Soc* 138(18):5731-5744.
5. Itkis DM, et al. (2015) Probing operating electrochemical interfaces by photons and neutrons. *ChemElectroChem* 2(10):1427-1445.
6. Grill V, Shen J, Evans C, Cooks RG (2001) Collisions of ions with surfaces at chemically relevant energies: Instrumentation and phenomena. *Rev Sci Instrum* 72(8):3149-3179.
7. Johnson GE, Hu Q, Laskin J (2011) Soft landing of complex molecules on surfaces. *Annu Rev Anal Chem* 4:83-104.
8. Cyriac J, Pradeep T, Kang H, Souda R, Cooks RG (2012) Low-energy ionic collisions at molecular solids. *Chem Rev* 112(10):5356-5411.
9. Verbeck G, Hoffmann W, Walton B (2012) Soft-landing preparative mass spectrometry. *Analyst (Lond)* 137(19):4393-4407.
10. Johnson GE, Gunaratne D, Laskin J (2016) Soft- and reactive landing of ions onto surfaces: Concepts and applications. *Mass Spectrom Rev* 35(3):439-479.
11. Rauschenbach S, et al. (2006) Electro spray ion beam deposition of clusters and biomolecules. *Small* 2(4):540-547.
12. Laskin J, Johnson GE, Prabhakaran V (2016) Soft-landing of complex ions for studies in catalysis and energy storage. *J Phys Chem C* 120:23305-23322.
13. Prabhakaran V, et al. (2016) Rational design of efficient electrode-electrolyte interfaces for solid-state energy storage using ion soft landing. *Nat Commun* 7:11399.
14. von Weber A, Baxter ET, White HS, Anderson SL (2015) Cluster size controls branching between water and hydrogen peroxide production in electrochemical oxygen reduction at Pt_n/ITO. *J Phys Chem C* 119(20):11160-11170.
15. Proch S, Wirth M, White HS, Anderson SL (2013) Strong effects of cluster size and air exposure on oxygen reduction and carbon oxidation electrocatalysis by size-selected Pt(n) (n ≤ 11) on glassy carbon electrodes. *J Am Chem Soc* 135(8):3073-3086.
16. MacFarlane DR, et al. (2016) Ionic liquids and their solid-state analogues as materials for energy generation and storage. *Nat Rev Mat* 1:15005.
17. Huang JY, et al. (2010) In situ observation of the electrochemical lithiation of a single SnO₂ nanowire electrode. *Science* 330(6010):1515-1520.
18. Zhang J, Xia Z, Dai L (2015) Carbon-based electrocatalysts for advanced energy conversion and storage. *Sci Adv* 1(7):e1500564.
19. Wibowo R, Aldous L, Jacobs RMJ, Manan NSA, Compton RG (2011) Monitoring potassium metal electrodeposition from an ionic liquid using in situ electrochemical X-ray photoelectron spectroscopy. *Chem Phys Lett* 509(1-3):72-76.
20. Tu Z, Nath P, Lu Y, Tikekar MD, Archer LA (2015) Nanostructured electrolytes for stable lithium electrodeposition in secondary batteries. *Acc Chem Res* 48(11):2947-2956.
21. Wang H, et al. (2012) In operando X-ray absorption fine structure studies of polyoxometalate molecular cluster batteries: Polyoxometalates as electron sponges. *J Am Chem Soc* 134(10):4918-4924.
22. Symes MD, Cronin L (2013) Decoupling hydrogen and oxygen evolution during electrolytic water splitting using an electron-coupled-proton buffer. *Nat Chem* 5(5):403-409.
23. Rogers EI, et al. (2008) Voltammetric characterization of the ferrocene/ferrocenium and cobaltocenium/cobaltocene redox couples in RTILs. *J Phys Chem C* 112(7):2729-2735.
24. Sel O, et al. (2013) Determination of the diffusion coefficient of protons in Nafion thin films by ac-electrogravimetry. *Langmuir* 29(45):13655-13660.
25. Sadakane M, Steckhan E (1998) Electrochemical properties of polyoxometalates as electrocatalysts. *Chem Rev* 98(1):219-238.
26. Lockett V, Horne M, Sedev R, Rodopoulos T, Ralston J (2010) Differential capacitance of the double layer at the electrode/ionic liquids interface. *Phys Chem Chem Phys* 12(39):12499-12512.
27. Taketa H, Katsuki S, Eguchi K, Seiyama T, Yamazoe N (1986) Electronic structure and redox mechanism of dodecamolybdophosphate. *J Phys Chem* 90(13):2959-2962.
28. López X, Carbó JJ, Bo C, Poblet JM (2012) Structure, properties and reactivity of polyoxometalates: A theoretical perspective. *Chem Soc Rev* 41(22):7537-7571.
29. Johnson GE, Laskin J (2010) Preparation of surface organometallic catalysts by gas-phase ligand stripping and reactive landing of mass-selected ions. *Chem Eur J* 16(48):14433-14438.
30. Johnson GE, Laskin J (2015) Soft landing of mass-selected gold clusters: Influence of ion and ligand on charge retention and reactivity. *Int J Mass Spectrom* 377:205-213.
31. Li S, Dixon DA (2006) Molecular and electronic structures, Brønsted basicities, and Lewis acidities of group VIB transition metal oxide clusters. *J Phys Chem A* 110(19):6231-6244.
32. Switzer EE, et al. (2013) Oxygen reduction reaction in ionic liquids: The addition of protic species. *J Phys Chem C* 117(17):8683-8690.
33. Johnson GE, Colby R, Engelhard M, Moon D, Laskin J (2015) Soft landing of bare PtRu nanoparticles for electrochemical reduction of oxygen. *Nanoscale* 7(29):12379-12391.
34. Johnson GE, Colby R, Laskin J (2015) Soft landing of bare nanoparticles with controlled size, composition, and morphology. *Nanoscale* 7(8):3491-3503.
35. Markovic NM, Gasteiger HA, Ross PN (1995) Oxygen reduction on platinum low-index single-crystal surfaces in sulfuric acid solution: Rotating ring-Pt(hk) disk studies. *J Phys Chem* 99(11):3411-3415.
36. Gasteiger HA, Kocha SS, Sompalli B, Wagner FT (2005) Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs. *Appl Catal B* 56(1-2):9-35.
37. Khan A, Lu X, Aldous L, Zhao C (2013) Oxygen reduction reaction in room temperature protic ionic liquids. *J Phys Chem C* 117(36):18334-18342.
38. Gunaratne KDD, et al. (2015) Design and performance of a high-flux electro spray ionization source for ion soft landing. *Analyst (Lond)* 140(9):2957-2963.
39. Johnson GE, Hadjar O, Laskin J (2011) Characterization of the ion beam focusing in a mass spectrometer using an IonCCD™ detector. *J Am Soc Mass Spectrom* 22(8):1388-1394.
40. Gunaratne KD, Prabhakaran V, Johnson GE, Laskin J (2015) Gas-phase fragmentation pathways of mixed addenda Keggin anions: PMo₁₂nW₄₀ 3⁻ (n = 0-12). *J Am Soc Mass Spectrom* 26(6):1027-1035.
41. Gunaratne KDD, et al. (2014) Controlling the charge state and redox properties of supported polyoxometalates via soft landing of mass-selected ions. *J Phys Chem C* 118(48):27611-27622.