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Scanning electrochemical microscopy (SECM) analysis of ionic polymer-metal composites (IPMCs) under applied electrical excitation: a case study of Pt- and Pd-IPMCs

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Abstract

Ionic polymer-metal composites (IPMCs) are electroactive polymers widely used in soft robotics and sensing applications due to their coupled electrochemical and electromechanical behavior. While macroscale characterization and performance testing of IPMCs have been widely reported, spatially resolved characterization at the microscale remains limited. In particular, scanning electrochemical microscopy (SECM) analysis of IPMCs under externally applied electrical excitation—where coupled electronic, ionic, and electromechanical processes occur—has not previously been reported. The objective of this work is to apply SECM to spatially probe local electrochemical responses in Pt- and Pd-based IPMCs under external electrical excitation. Comparative microstructural, mechanical, electrical, and electrochemical characterization shows that Pd-IPMC exhibits ~1.8-fold higher stiffness, ~33-fold higher surface electrode resistance, ~40% lower capacitance, ~64% lower swelling, and ~45% lower bending actuation compared to Pt-IPMC. These differences are attributed to Pd particle dispersion within the NafionTM membrane and a discontinuous electrode network. SECM measurements performed under sinusoidal, direct-current, and square-wave excitations demonstrate that tip current responses are influenced by probe-surface separation changes associated with electromechanically induced membrane swelling and contraction in the membrane domain, as well as by electron redistribution between the two electrode domains. Chronoamperometry under low-frequency excitation further reveals that, at small probe-surface separations, the SECM tip current is influenced by local cation concentration-related electrochemical effects, such as cation association with the redox mediator. These results demonstrate that SECM can spatially resolve coupled electromechanical deformation and localized electrochemical processes in IPMCs under external electrical excitation, providing information difficult to obtain using conventional bulk electrochemical characterization methods. This work provides a methodological foundation for applying SECM to investigate localized electromechanical deformation and cation-related electrochemical effects in electroactive polymer systems.

Abbreviations

IPMC	Ionic polymer-metal composite
SECM	Scanning electrochemical microscopy
UME	Ultramicroelectrode
DC	Direct current
AC	Alternating current

CV	Cyclic voltammetry
UME	Ultramicroelectrode
SEM	Scanning electron microscopy
EDS	Energy-dispersive x-ray spectroscopy
FFT	Fast Fourier transform

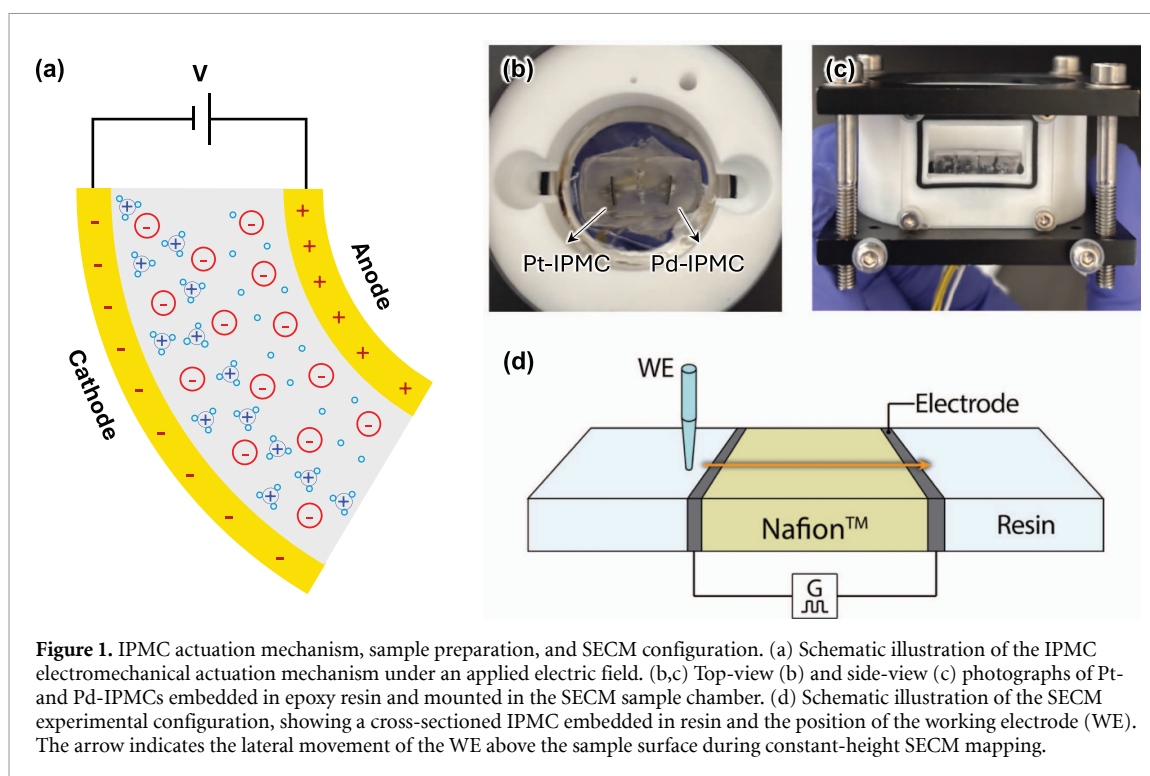
1. Introduction

IPMCs are electroactive polymer composites that exhibit coupled electromechanical actuation and sensing capabilities in hydrated environments. Due to these properties, IPMCs have been widely explored for underwater soft robotics [1–4], energy harvesting [5, 6], wearable devices [7, 8], and artificial muscle systems [9–11]. Structurally, an IPMC consists of an ion-exchange polymer membrane sandwiched between two metal electrode layers [12, 13]. The actuation mechanism of IPMCs originates from electrochemical transduction at the microscale. Upon application of an external electric potential across the electrodes, mobile cations within the membrane migrate toward the cathode under the applied electric field (figure 1(a)). Because these cations are hydrated, their migration is accompanied by transport of water molecules, resulting in localized swelling on the cathode side and contraction on the anode side. This asymmetric volume change produces macroscopic bending of the IPMC toward the anode, enabling electromechanical actuation. Conversely, mechanical deformation of the IPMC can induce redistribution of ions and charges, generating measurable electrical signals and enabling sensing functionalities such as underwater flow detection [14–16].

Numerous studies have focused on improving IPMC performance and identifying key parameters governing their electromechanical behavior. Among these, the interfacial area between the polymer membrane and the metal electrodes has been recognized as a critical factor, as it directly influences ion transport, water uptake, and charge accumulation [13, 17]. In particular, metal penetration into the polymer membrane increases the polymer–metal interfacial area, thereby enhancing electric double-layer capacitance and, in turn, improving bending actuation performance [18, 19]. Accordingly, a wide range of fabrication strategies has been developed to increase the effective polymer–metal interfacial area [13, 20–22]. These include membrane surface pretreatments to promote metal adhesion and penetration [23–25], the use of different electrode metals with distinct electrochemical and mechanical properties [26–30], and alternative reduction and plating methods designed to tailor electrode morphology and connectivity [13, 19, 22]. These polymer–metal interfaces are often characterized using SEM, which can directly visualize metal penetration and interfacial morphology in IPMC cross-section [18, 19, 24, 25].

In addition to microscale visualization of the polymer–metal interface, macroscale electrochemical properties and actuation performance of IPMC are commonly characterized for actuator and sensor applications. Actuation performance is typically evaluated in terms of tip displacement and blocking force under applied electrical stimuli [24, 30–33], and electrochemical behaviors are characterized using cyclic voltammetry (CV), from which an effective capacitance can be estimated [7, 18, 34]. In addition, electrochemical impedance spectroscopy is widely used to probe frequency-dependent electrochemical behaviors and enables separation of bulk ionic resistance, electrode–membrane interfacial impedance, and capacitive behavior associated with ion migration and electric double-layer dynamics, providing insight into electrochemical transduction beyond capacitance alone [35–38]. However, these electrochemical analyses are usually measured at macroscopic scale, and local heterogeneity in electrochemical reactivity is spatially averaged over IPMCs. Although these conventional characterization methods provide valuable bulk electrochemical and electromechanical information, they spatially average local electrochemical heterogeneity across the IPMC. As a result, localized electrochemical responses associated with electrode domains, membrane deformation, and ion redistribution under external electrical excitation remain difficult to directly probe.

SECM is a well-established technique for probing localized electrochemical activity at the micro- to nanometer scale [39–41]. An SECM system consists of an UME, typically with nanometer- to micrometer-scale diameter, positioned with precision near a sample surface immersed in a solution containing a redox mediator. The electrochemical current measured at the tip—during raster scanning at constant height or probe approach to the surface—reflects local electrochemical processes occurring in the vicinity of the probe. A commonly used operation mode is feedback mode, in which the SECM tip is biased to drive a diffusion-limited redox reaction in bulk solution, and the tip current changes by substrate-mediated regeneration or diffusion hindrance depending on the substrate type and tip–substrate separation. Above a conductive substrate, regeneration of the redox mediator at the



substrate surface enhances the tip current (positive feedback), whereas above an insulating substrate, diffusion of redox species to the tip is hindered, resulting in a decreased current (negative feedback). Because the feedback current is sensitive to both probe–surface separation and local electrochemical reactivity, SECM can provide useful information on electronic conductivity, surface reactivity, and local topography.

Recently, SECM has been applied to characterize IPMCs with different surface pretreatments, in which the IPMC membrane and electrode domains were spatially resolved, and the SECM tip current over electrode regions was correlated with electrode surface resistance [23]. This study demonstrated that SECM could be used to assess electrode network connectivity and local electrochemical heterogeneity across different domains in IPMC cross-sections [23]. In addition, Bath *et al* quantitatively investigated ion transport through NafionTM membranes using SECM [42]. In their work, ion transport through a Nafion-filled pore was controlled by a galvanostatically applied current across the membrane, and the SECM tip current measured above the pore was proportional to the local flux of an electroactive probe molecule emerging from the membrane, enabling estimation of diffusive and iontophoretic transport contributions, and further allowing determination of electroosmotic flow velocity and electroosmotic drag coefficients for solvent and solute transport. Together, these studies highlight the potential of SECM for probing cation migration and spatially resolved electrochemical behavior in ionomer-based systems such as IPMCs.

In this work, SECM analysis is applied to IPMCs under externally applied electrical excitation, where coupled electronic, ionic, and electromechanical processes occur. To the best of our knowledge, SECM investigations of IPMCs under externally applied electrical excitation have not previously been reported. The primary objective of this work is to provide an exploratory SECM-based analysis of IPMCs under electrical excitation and to establish a methodological foundation for applying SECM to electroactive polymers such as IPMCs. In addition, this study compares Pt- and Pd-based IPMCs to elucidate the influence of electrode material on local, microscale electrochemical and electromechanical transduction mechanisms. Pt- and Pd-IPMCs were selected because they exhibit distinct electrode morphologies, electrochemical properties, and mechanical behaviors, making them suitable model systems for investigating the influence of electrode structure on local SECM responses under electrical excitation. Prior to the SECM investigation, microstructural, mechanical, and electromechanical characterizations of Pt- and Pd-IPMCs are presented to establish fundamental differences between the two IPMC materials, thereby enabling more informed interpretation of the subsequent SECM analysis. SECM results are then presented under a range of applied electrical stimuli, including sinusoidal, direct-current, and square-wave excitations, to examine how local electrochemical responses evolve under dynamic electrical loading. This work demonstrates the sensitivity of SECM to electromechanically induced membrane deformation at

the probe–surface interface and discusses additional electrochemical contributions associated with local cation concentration, cation association with the redox mediator (ion pairing), and possible local viscosity changes. Overall, this study provides an initial framework for applying SECM to examine electromechanical deformation and ionic transport phenomena in IPMCs and related electroactive polymer systems.

2. Materials and methods

2.1. IPMC fabrication

Pt- and Pd-IPMCs were fabricated through three cycles of impregnation–reduction (primary plating) and two to three cycles of surface electroding (secondary plating). Detailed fabrication procedures, including NafionTM membrane surface pretreatment, are described in prior literature [23, 31, 43]. NafionTM 115 (Ion Power, Inc.) was used as the ionic membrane, and tetraamineplatinum (II) chloride hydrate and tetraaminepalladium (II) chloride monohydrate were used as the platinum and palladium electrode precursors, respectively. For the primary plating, lithium borohydride (LiBH_4) and sodium borohydride (NaBH_4) were used as reducing agents during the first two cycles and the final cycle of the primary plating, respectively. For the secondary plating, hydroxylamine hydrochloride and hydrazine were used for Pt-IPMC as the temperature of the precursor solution increased from 40 °C to 60 °C over 2.5 h, whereas only hydroxylamine hydrochloride was used for Pd-IPMC at room temperature to suppress bulk Pd reduction in solution and promote electrode formation on the membrane.

2.2. SECM analysis

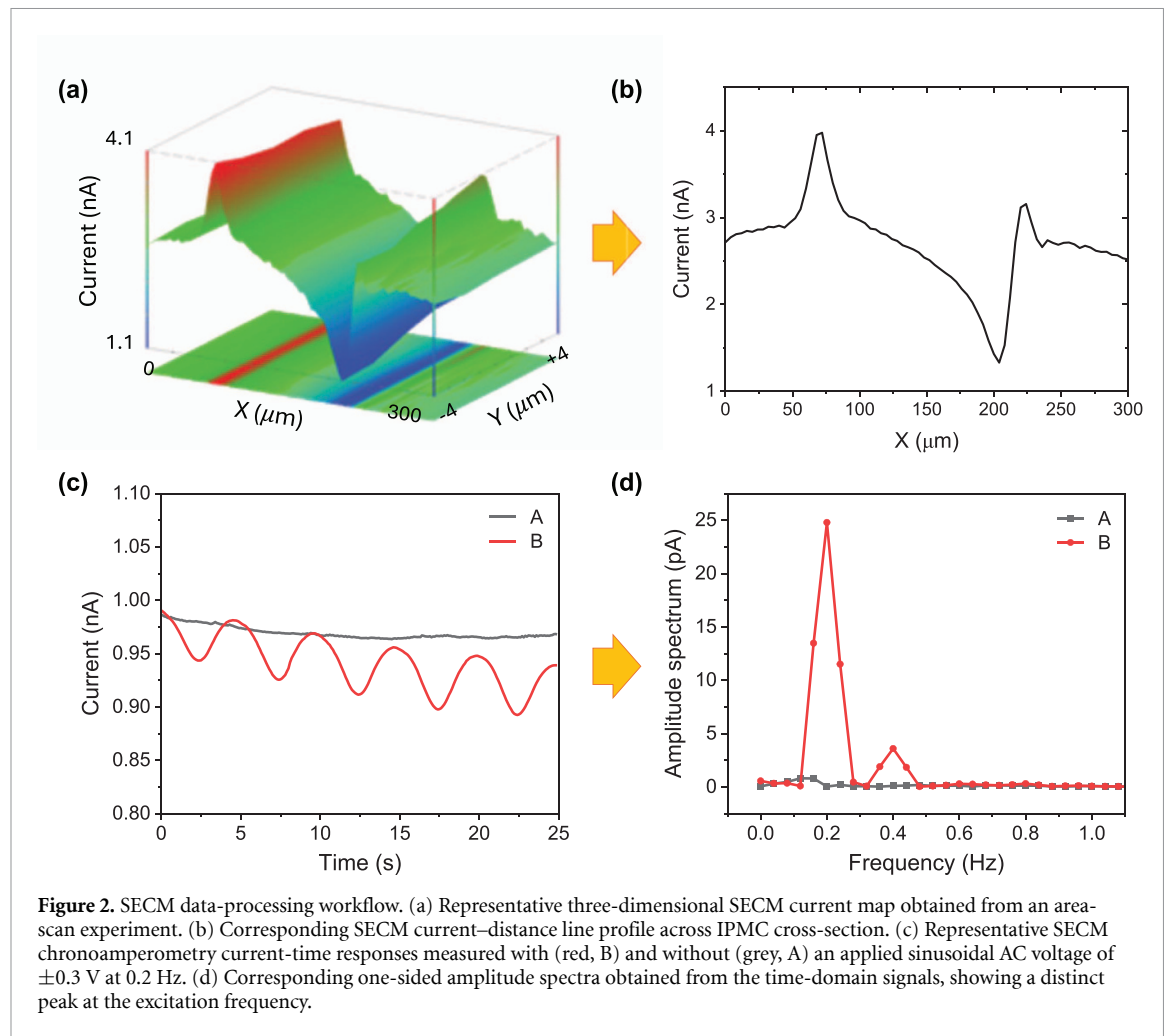
Fabricated Pt- and Pd-IPMCs were cut into ~5 mm wide and ~20 mm long, and electrical wires were soldered to the electrode surface prior to embedding in a hard epoxy resin (shore D hardness of 80). The hardened epoxy blocks were cross-sectioned to expose the IPMC cross-sections, and then re-embedded together in epoxy using a wide cylindrical mold to fit the SECM sample chamber, as shown in figures 1(b) and (c). The exposed IPMC/epoxy cross-sectional surface was further polished using #2000 sandpaper to obtain a smooth surface. Prior to SECM measurements, samples were immersed overnight in 1 M lithium nitrate (LiNO_3) solution to ensure near-equilibrium Li^+ ion exchange within the membrane.

SECM analysis was conducted using a scanning electrochemical workstation (M370, BioLogic) operated in feedback mode. A platinum disk UME with a diameter of 15 μm (SMP2045, Uniscan Instruments) was used as the working electrode (WE) for all experiments; a small Ag/AgCl electrode (reference electrode (RE)-1 S, Electrochemistry & Spectroelectrochemistry) was used as the RE; and a platinum sheet was used as the counter electrode (CE).

All electrodes were immersed in the SECM sample chamber filled with an electrolyte solution containing 5 mM potassium hexacyanoferrate (III)/potassium hexacyanoferrate (II) trihydrate as the redox mediator and 100 mM lithium chloride as the supporting electrolyte. Electrochemical measurements, including constant-height mapping, approach curve, and chronoamperometry, were conducted at room temperature under open-to-air conditions. A schematic illustration of SECM configuration and sample geometry is shown in figure 1(d). An SECM tip bias potential of 0.8 V was selected based on CV in the bulk solution (figure S1) and applied during all SECM experiments. External electrical excitation was applied to the electrodes of the embedded IPMC via wires soldered to the IPMC electrode surfaces using a signal generator (SDG1025, Siglent).

The SECM current–distance profiles across IPMC cross-sections (figure 2(a)) were obtained by averaging five individual line scans extracted from SECM area-scan measurements (figure 2(b)). The area scans were performed in sweep scan mode over a 300 $\mu\text{m} \times 8 \mu\text{m}$ region, with spatial resolutions of 4 μm per point in the X direction and 2 μm per point in the Y direction. The scan velocity, line delay, and return velocity were 20 $\mu\text{m s}^{-1}$, 2 s, and 500 $\mu\text{m s}^{-1}$, respectively, resulting in a total acquisition time of approximately 2 min for each area scan. The five line scans collected at $Y = +4, +2, 0, -2$, and $-4 \mu\text{m}$ in the area scans, spanning the electrode–membrane–electrode region, were averaged into line profiles (figure 2(a) and (b)). Averaging was employed to mitigate the influence of local heterogeneity in the Y direction. Although consecutive area-scan experiments were initiated within ~5 s, the acquisition time and unavoidable variability in scan initiation limit quantitative time-resolved analysis of the area-scan data. Nevertheless, this approach is sufficient to capture qualitative trends in SECM current responses under different externally applied electrical signals.

Chronoamperometry experiments were performed under a bias potential of 0.8 V with a sampling rate of 10 Hz over a duration of 25 s. Measurements were conducted at both the NafionTM membrane



and resin regions, at different probe heights, while applying an external sinusoidal AC voltage (none, ± 0.3 V, and ± 0.6 V) at a frequency of 0.2 Hz. The resulting current-time responses were transformed into the frequency domain to examine whether the measured signals exhibited oscillatory components corresponding to the applied sinusoidal excitation (figures 2(c) and (d)). Frequency-domain analysis was carried out using a custom Python script (see **supplementary information**) implementing a one-sided real-valued fast Fourier transform (rFFT) [44]. Prior to the Fourier transform, the raw current signals were detrended by subtracting a polynomial baseline fit, followed by mean removal, and subsequently multiplied by a Hann window to suppress spectral leakage. The resulting amplitude spectra were normalized to enable comparison of spectral peaks across different probe heights and measured regions.

Approach curves were acquired to estimate how far the probe is from the cross-sectioned IPMC surface. The tip current was measured every 10 μm as the probe approached the substrate over a total distance of 150 μm using step-scan mode, with an acquisition pre-delay of 0.5 s at each step. Approach curves obtained at the center of the membrane were fitted using an analytical approximation for diffusion-limited negative feedback [45]:

$$I_T(L) = 1/[a_1 + a_2/L + a_3 \exp(a_4/L)] + a_5 \times L/(a_6 + L)$$

where I_T is the normalized tip current defined as $I_T = i_T/i_\infty$ with i_∞ being the bulk steady-state micro-disk current, and $L = d/a$ is the dimensionless tip-substrate separation, where d is the physical separation distance and a is the tip disk radius. The probe-surface separation distances were determined from the fitted approach curves.

2.3. SEM and EDS

The fabricated IPMCs were dried and cross-sectioned using a razor blade, followed by gold sputter coating using a mini sputter coater (SC7620, Emitech). Cross-sectional images were acquired using a TESCAN VEGA scanning electron microscope operated at an accelerating voltage of 15 keV in secondary

electron and backscattered electron modes. EDS analysis was performed using an Ultim Max 65 EDS detector (Oxford Instruments) attached to the SEM system.

2.4. Physical and mechanical characterization: swelling and tensile testing

For swelling measurements, Li⁺-exchanged IPMCs were cut into strips (5 mm × 20 mm) and dried overnight. The thicknesses of the dried and hydrated samples were measured before and after immersing in deionized water for 5 min. The swelling ratio was calculated as the relative change in thickness upon hydration, defined as the difference between the hydrated and dry thicknesses normalized by the dry thickness [23].

The stress–strain relationships of the fabricated IPMCs were measured using a dynamic mechanical analyzer (Pyris Diamond DMA, PerkinElmer). IPMCs were cut into rectangular strips (5 mm × 20 mm) and then mounted in the DMA tensile test fixture with a gauge length of 15 mm. The samples were fully hydrated and stretched by $\sim 300\ \mu\text{m}$ at a displacement rate of $150\ \mu\text{m min}^{-1}$ under L-controlled mode.

2.5. Electrochemical characterization: CV and surface resistance

CV measurements of the fabricated IPMCs were performed using a PGZ 402 potentiostat/galvanostat (Radiometer Analytical) controlled by VoltaMaster 4 software. Rectangular IPMC strips (10 mm wide and 40 mm long) were used for the measurements. The top 10 mm × 10 mm area of each strip was electrically contacted with a platinum sheet using a clamp, and the entire strip was immersed in water during the measurements. CV measurements were conducted in a two-electrode configuration, with scan rates of 10, 20, and 30 mV s^{−1}. Although the obtained CV curves did not exhibit ideal rectangular behavior [46, 47], the capacitance (*C*) was calculated from the enclosed CV area using the following equation:

$$C = \frac{\int I(V) dV}{2v\Delta V}$$

where *v* is the scan rate and ΔV is the potential window. Capacitance per unit area was calculated by normalizing the capacitance by the surface area of the IPMC strips (4 cm²). IPMC surface resistance was measured using a digital multimeter with two probes separated by approximately 20 mm.

2.5.1. Bending actuation tests

To evaluate IPMC actuation performance, the tip displacement of 10 mm-wide and 40 mm-long IPMC strips under an applied sinusoidal AC voltage of $\pm 0.61\ \text{V}$ at 500 mHz was measured using a laser displacement sensor (optoNCDT-1401, Micro-Epsilon). The sinusoidal AC signal was generated using a signal generator (SDG1025, Siglent), amplified by a power amplifier (LVC608, AE Techtron), and applied to the IPMC strips. The laser beam was positioned approximately 5 mm above the free end of the IPMC strips. The current response was measured using a resistor connected in series with the IPMC strips in the circuit. The input voltage, current, and displacement signals were recorded using a data acquisition system (DAQ6510, Keithley).

3. Results and discussion

3.1. Fundamental differences between fabricated Pt- and Pd-IPMCs

IPMCs fabricated with platinum and palladium metals exhibit noticeable differences in microstructure within the polymer membrane region. As shown in figure 3, SEM-EDS analysis reveals that Pd-IPMC has a pronounced Pd particle-rich region within the NafionTM membrane (arrows in figure 3(f)), whereas Pt-IPMCs exhibit little to no detectable Pt within the membrane interior. This Pd particle-rich region consists of dispersed Pd particles distributed over the entire membrane domain (figure S2(c)), rather than a continuous metal layer extending inward from the electrode layers. The Pd particle-rich region likely results from the higher chemical reactivity of Pd precursor compared to Pt precursor during the impregnation–reduction process. In a prior study by Kim *et al* immersion of NafionTM in a Pd salt solution for only 2 h resulted in penetration depths of several micrometers [27]. In the present fabrication process, the overnight soaking in Pd precursor solution and the three cycles of primary plating using strong reducing agents are therefore thought to result in the formation of a large Pd particle-containing region within the membrane.

Despite the presence of this broad Pd particle-rich region, Pd-IPMCs did not exhibit enhanced electrochemical capacitance. The cyclic voltammograms in figure 4(a) show that Pd-IPMC exhibits a smaller enclosed area than Pt-IPMC. The calculated areal capacitances were 4.7 mF cm^{−2} for Pd-IPMCs and

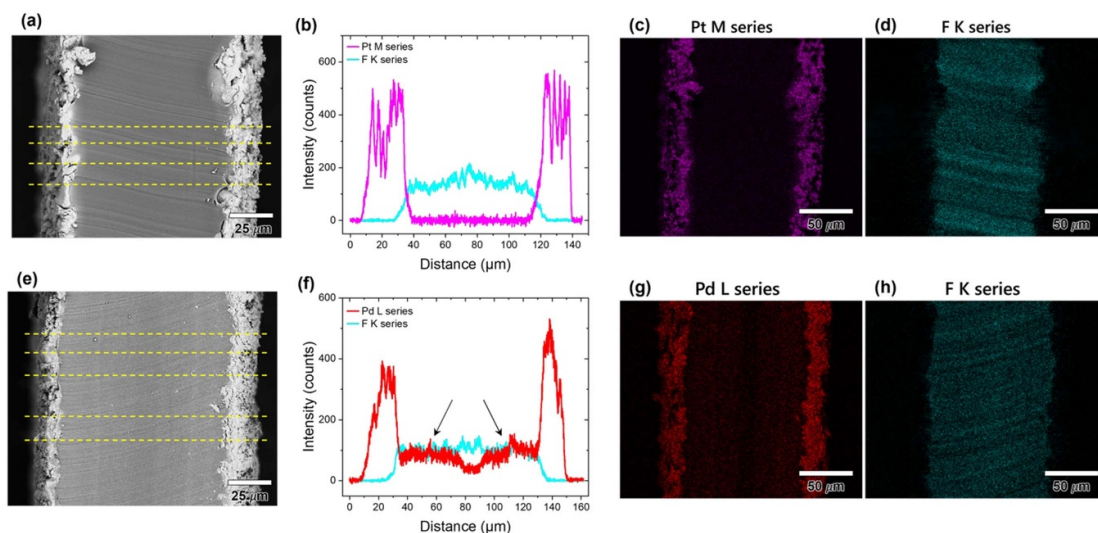


Figure 3. SEM-EDS analysis of Pt-IPMC and Pd-IPMC cross-sections. (a), (e) Cross-sectional SEM images of a Pt-IPMC (a) and Pd-IPMC (e). Dashed lines indicate the line-scan paths used for EDS line profiles. (b), (f) Averaged EDS line profiles showing the spatial distributions of the Pt (M series), Pd (L series), and F (K series) across the IPMC thickness in Pt-IPMC (b) and Pd-IPMC (f). The arrows in (f) highlight the presence of Pd-particles within polymer membrane. (c), (d), (g), (h) EDS elemental maps of Pt-IPMC (c), (d) and Pd-IPMC (g), (h). The elemental maps show the Pt and Pd electrode regions and the fluorine-rich NafionTM membrane region.

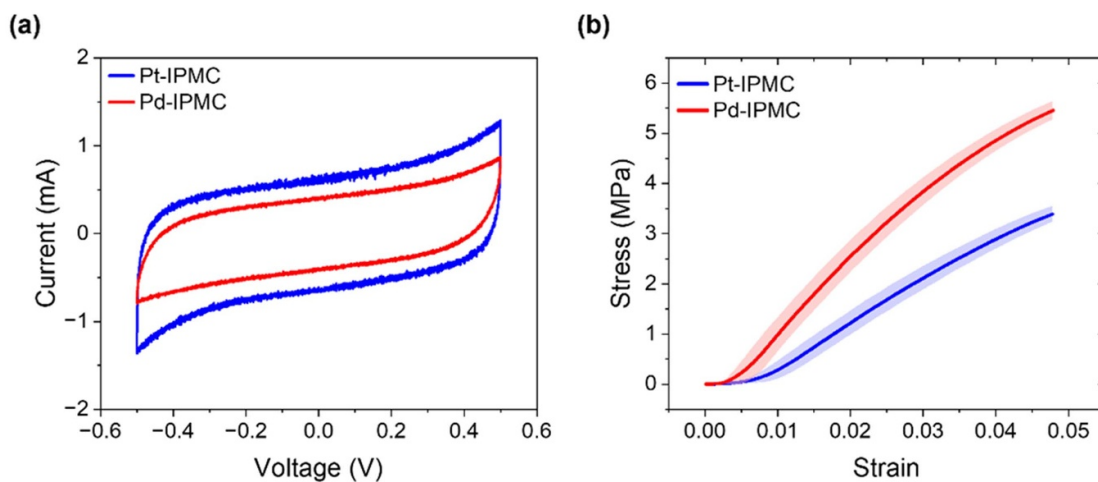
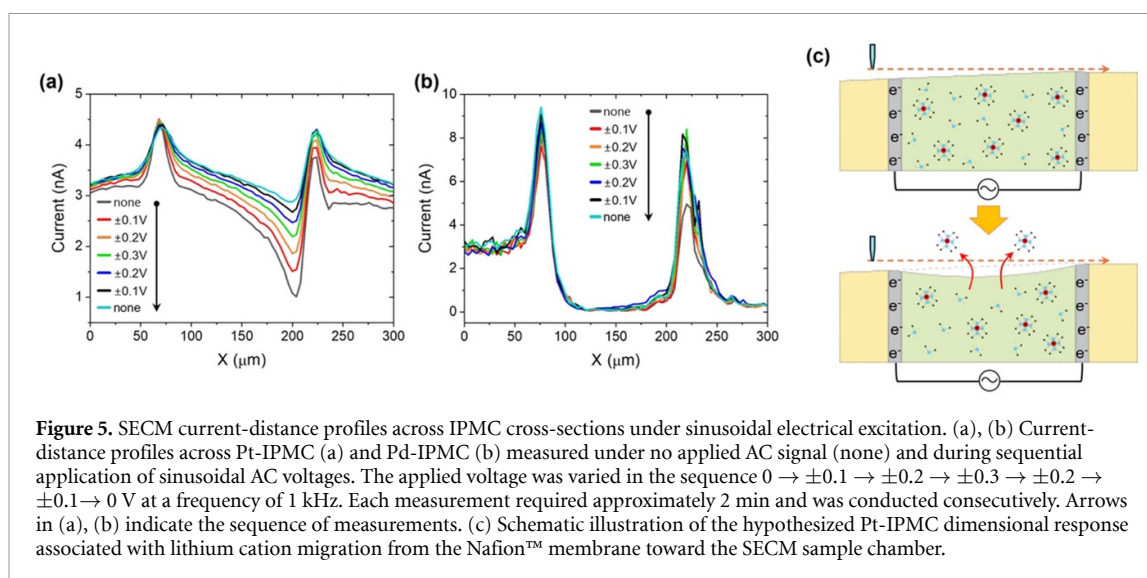


Figure 4. Cyclic voltammetry (CV) responses and tensile testing of fabricated IPMCs. (a) Representative cyclic voltammograms of Pt-IPMC and Pd-IPMC at a scan rate of 20 mV s^{-1} . (b) Averaged stress-strain curves of Pt-IPMC ($n = 4$) and Pd-IPMC ($n = 5$), with elastic moduli of 0.70 MPa and 1.28 MPa , respectively, calculated from the 0% – 3% strain region. The measured stress magnitude for Pt-IPMC is consistent with previously reported tensile measurements [50].

7.9 mF cm^{-2} for Pt-IPMCs, which are within the range reported for IPMCs [48, 49]. The larger areal capacitance of Pt-IPMCs compared to Pd-IPMC was consistently observed across different scan rates in figure S3. Although metal penetration into polymer membranes is known to be associated with increased polymer–metal interfacial area and enhanced electric double-layer capacitance [18, 19], the results here indicate that the broadly dispersed Pd particles located deep within the membrane do not effectively contribute to the electrochemically active interfacial area. This interpretation is further supported by the significantly higher surface electrode resistance of Pd-IPMCs ($80.2 \pm 24.5 \Omega$, $n = 12$) compared to Pt-IPMCs ($2.4 \pm 0.4 \Omega$, $n = 12$) even though the formed electrode thicknesses are similar (figures 3(a), (e), S2(a) and (b)), suggesting that the Pd particles within the membrane are electrically and spatially disconnected from the surface electrode network [23, 24]. As a result, these particles contribute minimally to charge transfer and electric double-layer formation and thus have limited impact on surface conductivity or electrochemical actuation efficiency.

In contrast to the limited impact on electrochemical performance, the Pd particle-rich region influences the mechanical behavior of the IPMC. Stress–strain measurements show that Pd-IPMCs exhibit



approximately 1.8-fold higher tensile stiffness in the 0%–3% strain region compared to Pt-IPMCs (figure 4(b)). This trend is consistent with prior studies demonstrating that embedded fillers significantly enhance the mechanical properties of polymer composites [51–54]. Furthermore, Pd-IPMC displayed significantly reduced swelling upon hydration ($\sim 8\%$) compared to Pt-IPMCs ($\sim 22\%$), as summarized in table S1, likely due to the stiffer nature of the Pd-IPMC. The reduced swelling is consistent with the low areal capacitance of Pd-IPMC, which is related to electric double-layer formation through hydrated cation migration [55].

Consistent with the electrochemical, swelling, and mechanical differences, Pd-IPMC exhibited inferior bending actuation performance. Bending actuation tests show that Pt-IPMC exhibited ~ 1.8 -fold larger tip displacement and ~ 2.5 -fold higher current flow compared to Pd-IPMCs (figure S4). Bending actuation reflects the combined effects of capacitance, stiffness, and electrode conductivity: lower electrochemical capacitance limits the accumulation of hydrated cations at the electrode–membrane interface, leading to smaller volume expansion; higher stiffness mechanically constrains deformation; and lower electrode conductivity leads to higher potential drop across the electrodes, thereby limiting current flow [23, 24].

3.2. SECM analysis under sinusoidal AC external signal

Figure 5 presents SECM current–distance profiles across Pt- and Pd-IPMC cross-sections obtained under sequentially increasing and decreasing sinusoidal AC excitation amplitudes. High-frequency sinusoidal electrical signals (>1 kHz) were first applied to remove potential imbalances of static charge in the electrode layers that may arise from sample preparation and embedding. Notably, the two electrode-related current peaks in the Pd-IPMC were initially asymmetric (figure 5(b)) but became more comparable in magnitude upon application of the AC excitation, suggesting redistribution of electronic charge between the two electrode domains. As the applied potential alternates polarity much faster than the SECM current acquisition rate (5 Hz), transient charge distribution is not reflected in SECM current-distance profiles, and the application of high-frequency sinusoidal excitation is thought function as evenly distributing electrons between the two electrodes. The overall profile shape is consistent with prior SECM measurements of IPMCs obtained without external electrical excitation [23]: the two broad maxima correspond to the conductive metallic electrode layers, where redox regeneration is favored, whereas the low-current regions between and outside the electrodes correspond to the insulating Nafion™ membrane and epoxy resin, respectively, where diffusion of redox species is hindered.

Despite the same excitation procedure, Pt- and Pd-IPMCs showed distinct evolution of the SECM current profiles over the measurement sequence. Although the sequentially increasing and decreasing AC excitation was applied to check whether the excitation amplitude influences the profile beyond the uniform charge redistribution, a pronounced increase in current intensity in the membrane domain was observed in Pt-IPMC (figure 5(a)). This gradual increase continued across the measurement sequence and was independent of the applied AC amplitude, indicating that it reflects a time-dependent physical change rather than effect of the electrical excitation. Because the SECM current is sensitive to probe–surface separation and the membrane is electrically insulating, this behavior must be due to gradual membrane shrinkage. Such shrinkage likely arises from redistribution of lithium cations between the membrane and the surrounding electrolyte, as schematically illustrated in figure 5(c). This behavior may

be further influenced by ion exchange between Li^+ initially present in the membrane and K^+ ions in the solution, which are present at relatively high concentration as counterions of the redox mediator. Because the water uptake of K^+ -exchanged IPMCs is lower than that of Li^+ -exchanged IPMCs [38], partial replacement of Li^+ by K^+ would be expected to promote membrane shrinkage. In contrast, Pd-IPMC did not exhibit a comparable time-dependent current intensity increase in the membrane domain. This is likely due to the higher mechanical stiffness of Pd-IPMC membrane resulting from the Pd particles distributed throughout the membrane (figure 3(f)), which mechanically constrains membrane shrinkage. This interpretation is further supported by the limited polymer shrinkage observed upon drying of hydrated, cross-sectioned IPMCs in figure S2.

Additional features are observed in the current–distance profiles that are primarily attributed to experimental and geometrical factors. The localized asymmetry in current profiles in the membrane domain of Pt-IPMC (e.g. the dip near $X \approx 200 \mu\text{m}$ in figure 5(a)) is likely caused by a combination of the sweep-scan velocity effects and nonuniform surface topography introduced during sample preparation [23], as supported by the longer current decay tail observed on one side of the profile. Additionally, the asymmetric current levels observed in the resin regions on the left ($X = 0 \mu\text{m}$) and right ($X = 300 \mu\text{m}$) sides of Pd-IPMC (figure 5(b)) are attributed to slight sample surface tilt during mounting or polishing. Furthermore, the higher current intensity at the electrode domains and near-zero current in the membrane domain of Pd-IPMC suggest that the SECM probe scanned at a smaller probe–surface separation near the Pd-IPMC cross-section surface.

3.3. SECM under DC biased potential

SECM current profiles across IPMC cross-sections showed distinct changes under an applied DC bias. The application of a DC bias was initially intended to probe whether SECM could detect the redistribution of Li^+ cation across the NafionTM membrane. Alkali metal cations in the supporting electrolyte are known to play a role in hexacyanoferrate redox chemistry by reducing anion–anion repulsion and, in some cases, forming transient cation-bridged activation complexes that facilitate electron transfer, effectively acting as catalysts [56, 57]. In the absence of alkali metal cations, the self-exchange rate constant of the ferri/ferrocyanide redox couple decreases by nearly two orders of magnitude [57]. Accordingly, application of a DC bias was expected to separate cations and hexacyanoferrate anions across the membrane, potentially leading to measurable changes in SECM tip current that could reflect local cation distribution within the membrane. However, figure 6 shows that the observed SECM current changes were dominated by responses in the electrode domains, and no clear DC-potential-dependent features were observed within the membrane interior or at the membrane–electrode interface for either Pt- or Pd-IPMCs.

Nonetheless, the electrode domain responses are consistent with SECM oxidation feedback mode behavior. Under +0.8 V tip bias, the oxidation reaction ($\text{Fe}(\text{CN})_6^{4-} \rightarrow \text{Fe}(\text{CN})_6^{3-} + e^-$) occurs at the tip, and the resulting current is enhanced over conductive substrate through redox regeneration governed by electron-transfer kinetics at the substrate–solution interface. In figures 6(a) and (c), when a positive bias was applied to the right electrode (relative to the left electrode/ground), the current intensity increased in the left electrode domain, whereas it decreased in the right electrode domain. This behavior is likely due to electronic charge redistribution between the two IPMC electrodes under the applied bias potential, affecting the local ability to regenerate the redox mediator at the SECM probe. Above the left electrode, accumulated electrons facilitate electron transfer to the oxidized mediator, enhancing mediator regeneration and leading to an increase in SECM current. Conversely, above the right electrode, relative electron depletion reduces the availability of electrons for mediator regeneration, resulting in a decreased SECM current. A corresponding trend was observed when a negative bias was applied (figure S5).

However, the tip current over the electrode domain did not immediately return to the initial status upon removal of the DC bias. The increased current intensity showed little recovery upon bias removal (left electrode in figures 6(b) and (d)). In contrast, the decreased current intensity partially recovered over time but did not fully return to the initial level over three consecutive post-bias measurements (~ 6 min) (right electrode in figures 6(b) and (d)). This delayed and incomplete recovery likely reflects slow redistribution of lithium cations at the electrode–membrane interface, which maintains interfacial polarization and thereby retards relaxation of the electronic charge distribution in the electrode, preventing immediate return to the initial state. A qualitatively similar relaxation behavior was observed when a negative bias was applied (figure S5). For Pd-IPMC, bias potential of 0.05–0.2 V produced minimal change, which may be attributed to the higher surface electrode resistance and reduced electrical connectivity of the Pd electrode network, as discussed earlier. Accordingly, bias potentials of 0.2–0.6 V were applied (figures 6(c) and (d)).

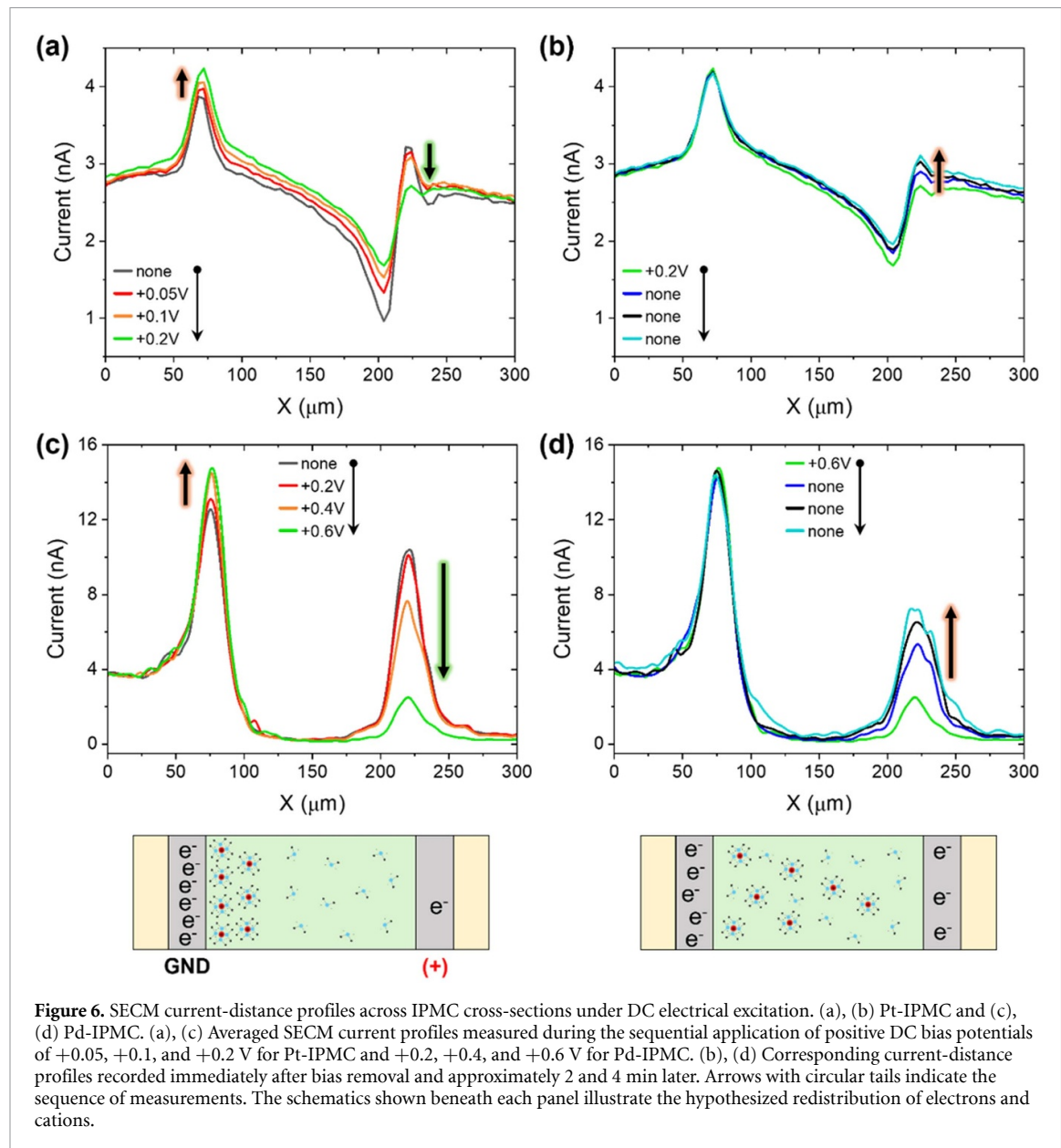


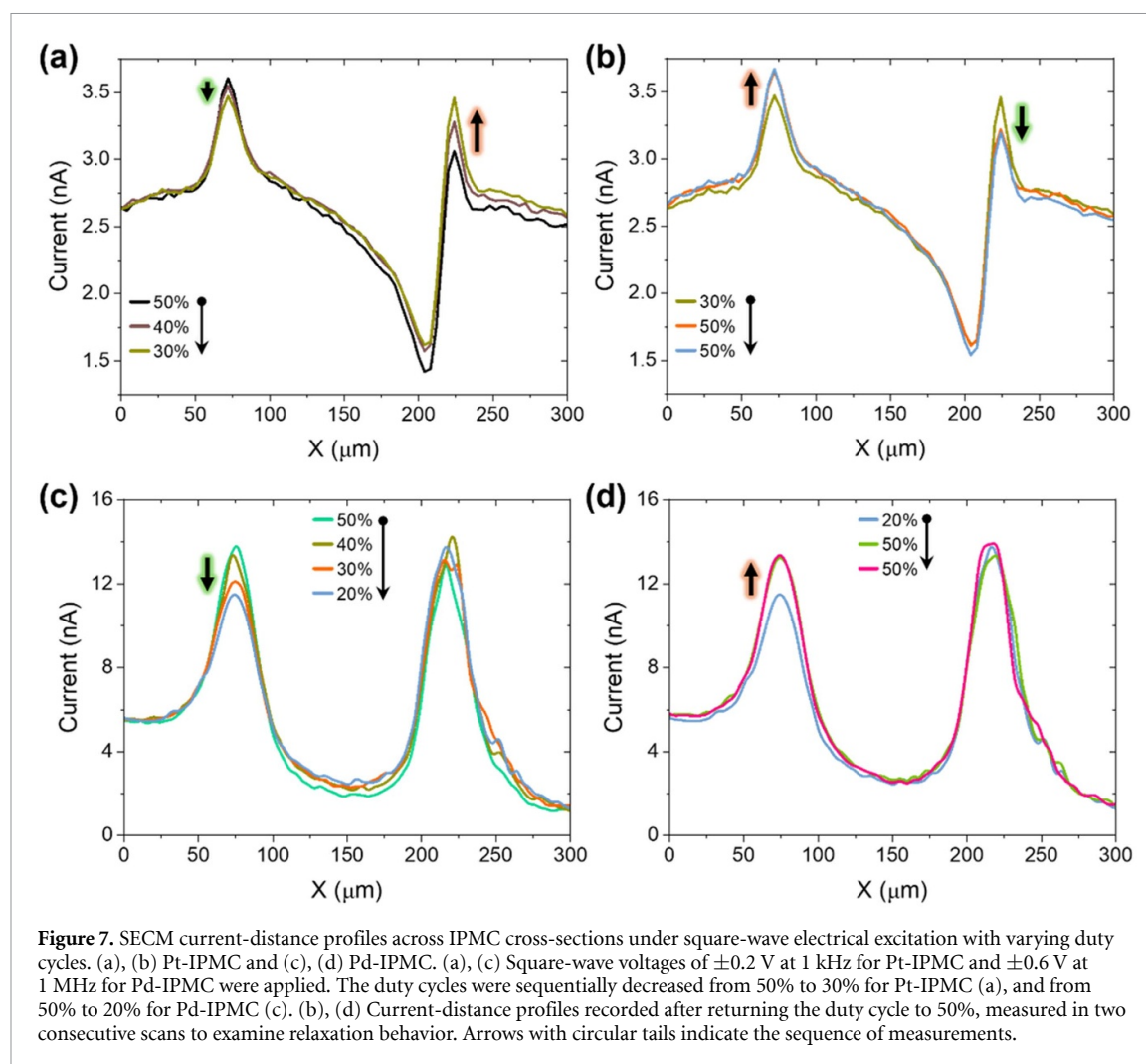
Figure 6. SECM current-distance profiles across IPMC cross-sections under DC electrical excitation. (a), (b) Pt-IPMC and (c), (d) Pd-IPMC. (a), (c) Averaged SECM current profiles measured during the sequential application of positive DC bias potentials of +0.05, +0.1, and +0.2 V for Pt-IPMC and +0.2, +0.4, and +0.6 V for Pd-IPMC. (b), (d) Corresponding current-distance profiles recorded immediately after bias removal and approximately 2 and 4 min later. Arrows with circular tails indicate the sequence of measurements. The schematics shown beneath each panel illustrate the hypothesized redistribution of electrons and cations.

3.4. SECM under squared AC signal with various duty cycle

SECM current profiles exhibited measurable responses to changes in duty cycle under square-wave excitation. Although the magnitude of the change is relatively small, the current intensity in the left electrode domain decreased, while the intensity in the right electrode domain increased, as the duty cycle was reduced from 50% to 30% in Pt-IPMC (figure 7(a)). This behavior arises because the duty cycle determines the relative duration of positive and negative bias within each square-wave period, thereby modulating the net electronic polarization of the electrode pair. Consistent with this interpretation, the trend is reversed when the duty cycle is increased from 50% to 70% (figure S6(a)).

In contrast to DC bias, no delayed relaxation behavior was observed under square-wave excitation. When the duty cycle was returned to 50%, the current-distance profile immediately recovered to the initial 50% profile and remained stable (figure 7(b) and figure S6(b)). This rapid recovery is attributed to the continuous alternation of electrode polarity in square-wave excitation, which prevents sustained electronic polarization or ionic accumulation at the electrode-membrane interfaces.

Pd-IPMC exhibited qualitatively similar SECM current responses under square-wave excitation with varying duty cycles (figures 7(c) and (d)). However, deviations from the overall trend were observed, such as relatively weak change in current intensity above the right electrode in figures 7(c) and (d) and figure S6(d). These deviations are likely associated with the discontinuous and porous Pd electrode network, which can lead to inefficient electronic charge redistribution under rapidly alternating square-wave excitation. Nevertheless, as in Pt-IPMC, the Pd-IPMC current profiles immediately returned to the initial

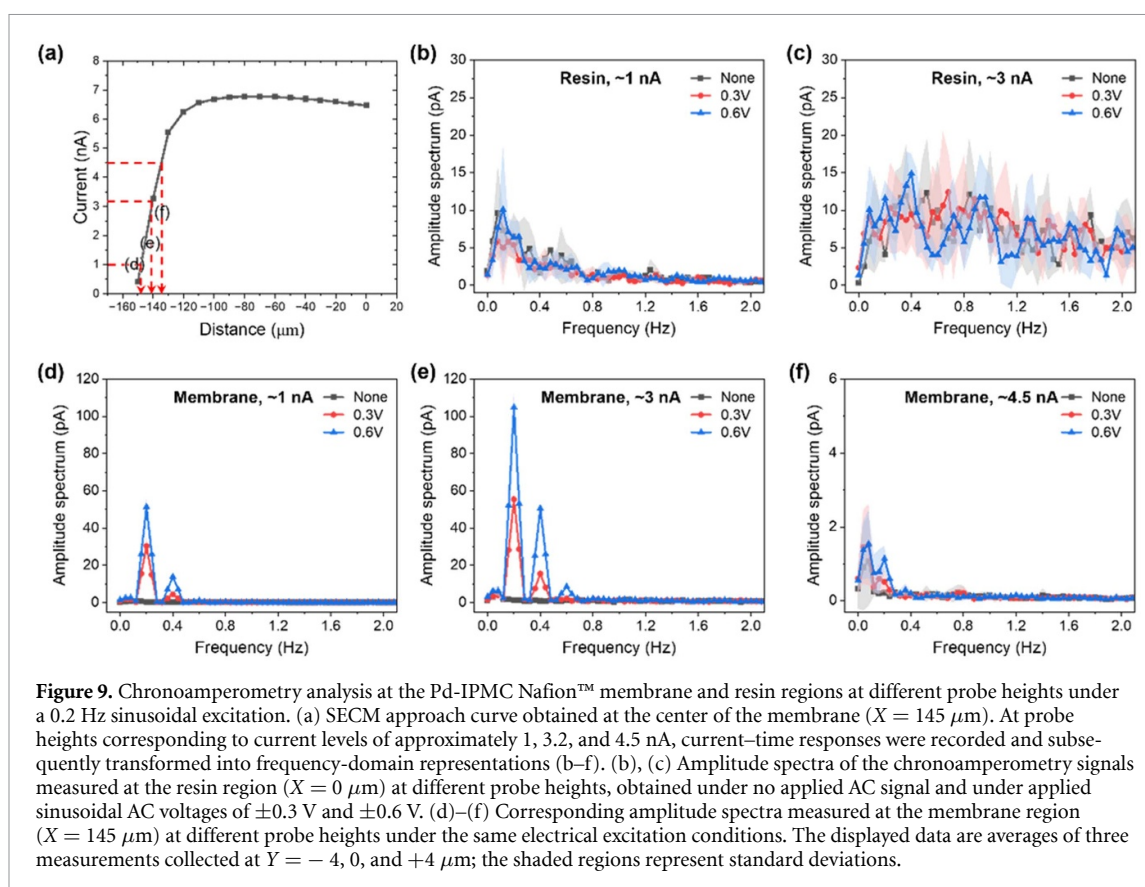
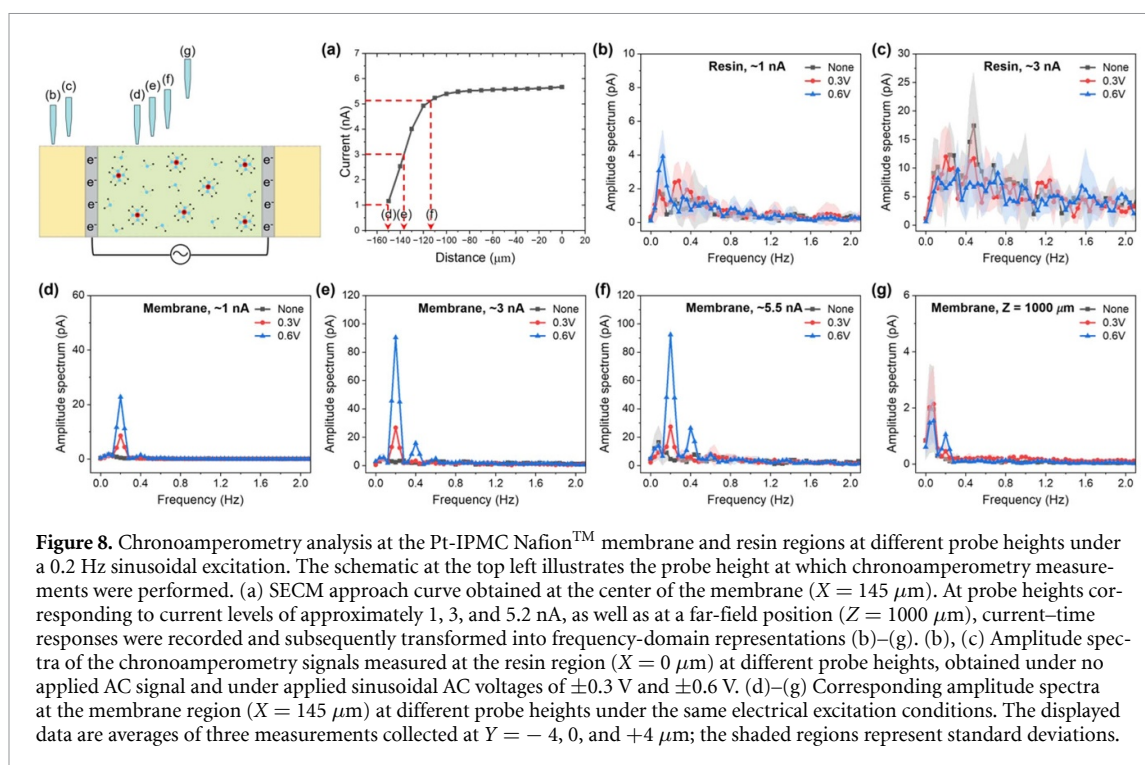


50% duty-cycle state when the duty cycle was restored to 50% (figure 7(c) and figure S6(c)), indicating the absence of long-lived polarization effects under square-wave operation.

3.5. Chronoamperometry analysis at membrane domain

The response of IPMCs to external electrical excitation was further investigated using chronoamperometry under sinusoidal excitation at 0.2 Hz. Chronoamperometry enables probing local electrochemical responses at a fixed location over time within the effective diameter of the SECM WE, without artifacts associated with lateral sweep scanning and surface topography. To determine the probe-surface separation, SECM approach curves were first measured at the membrane center (figure 8(a) and figure 9(a)), and chronoamperometry measurements were subsequently performed at probe heights corresponding to current levels of approximately 1, 3, 4.5, and 5.2 nA (figures 8(b)–(g) and figures 9(b)–(f)). Notably, for Pd-IPMC (figure 9(a)), the far-field tip current measured above the membrane was higher than the steady-state diffusion-limited current obtained under a 0.8 V tip bias in bulk solution (figure S1), and the current decreased more rapidly as the probe approached the surface compared to Pt-IPMC (figure 8(a)). This behavior may arise from partial redox-mediator regeneration by Pd particles dispersed within the membrane (figure 3), suggesting that these particles locally act as weakly electrochemically active domains.

Chronoamperometry measurements clearly captured the response to sinusoidal excitation at 0.2 Hz. At the resin region, no distinct peak at 0.2 Hz was observed under applied AC amplitudes from 0 to ± 0.6 V (figure 8s(b)–(c) and figures 9(b)–(c)), even when the probe was positioned close to the surface (corresponding to a current level of ~ 1 nA). In contrast, at the membrane region, a pronounced peak at 0.2 Hz corresponding to the fundamental excitation frequency was observed, accompanied by weaker peaks at 0.4 and 0.6 Hz corresponding to the second- and third-harmonic responses. The presence of higher harmonics indicates a nonlinear current response to the applied sinusoidal excitation.



This behavior is consistent with the fact that the SECM tip current under feedback mode exhibits a non-linear dependence on the tip–substrate separation [45, 58]. While the effect of local cation concentration on redox reactions cannot be excluded at this stage, the observed frequency-domain response is thought to be associated with periodic changes in probe–surface separation arising from membrane swelling and contraction under electrical excitation.

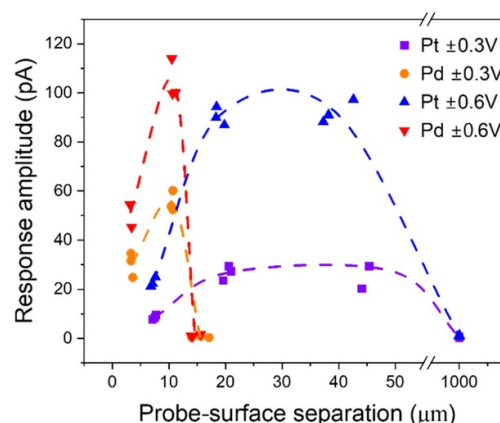


Figure 10. Probe–surface separations and corresponding amplitudes of sinusoidal current responses. Probe–surface separations were estimated from fitted approach curves (figure S8), and response amplitudes correspond to the magnitude of the fundamental frequency component at 0.2 Hz. Data are shown for excitation amplitudes of ± 0.3 V and ± 0.6 V.

The magnitude of the sinusoidal current response varied with probe height. When the probe was positioned close to the membrane surface (current level of ~ 1 nA in figure 8(d) and figure 9(d)), the response amplitude was smaller than that observed at larger probe–surface separation (current level of ~ 3 nA in figure 8(e) and figure 9(e)). This trend is opposite to what would be expected if the response were governed solely by tip–substrate distance modulation, as the approach curves (figure 8(a) and figure 9(a)) show a steeper current gradient at smaller separations. This indicates the presence of additional factors influencing the tip current near the membrane surface, such as cation association of the redox mediator with alkali cations (ion-pairing) and altered diffusion kinetics due to locally increased viscosity.

Locally enhanced viscosity arising from high concentrations of hydrated cations may reduce tip current by slowing mass transport. Indeed, the steady-state tip current monotonically decreased by approximately 1 nA as lithium-ion concentration increases from 0 to ~ 1.6 M in bulk solution (figure S7). However, if local viscosity effects alone dominated, a larger current oscillation amplitude would still be expected near the surface because diffusion hindrance from small tip–surface separation upon swelling would be amplified by viscosity. This is inconsistent with the experimentally observed reduction in response amplitude at small separations (current level of ~ 1 nA).

In addition to viscosity effects, alkali metal cations are known to facilitate ferri/ferrocyanide redox reactions by reducing anion–anion repulsion and forming transient cation-bridged activation complexes [56, 57]. A locally elevated cation concentration near the membrane surface could therefore enhance the redox reaction at the probe tip when the probe–surface separation decreases during membrane swelling, partially compensating for diffusion hindrance and distance-dependent current modulation. The net result would be a reduced oscillation amplitude despite the smaller probe–surface separation. It should be noted that lithium ions possess a much higher hydration energy than potassium ions [59, 60], forming larger and more strongly hydrated clusters that are less effective in facilitating redox reactions (figure S7), whereas potassium ions exhibit weaker hydration and more effectively catalyze the redox process [56]. Given the high K^+ concentration present in the system and its partial presence within the NafionTM membrane through cation exchange, this effect is plausible. Consequently, the reduced oscillation amplitude observed at probe positions corresponding to a current level of ~ 1 nA most plausibly reflects modulation of the SECM tip current by ion-pairing effects associated with locally elevated cation concentrations near the membrane surface.

Pt-IPMC and Pd-IPMC exhibited distinct current responses in the chronoamperometry experiments. Figure 10 summarizes the probe–surface separations obtained from fitted approach curves (figure S8), along with the corresponding amplitudes of the sinusoidal SECM current responses. Although the available data points are limited, a non-monotonic trend is observed, in which the response amplitude initially increases and then decreases with increasing probe–surface separation for both Pt-IPMC and Pd-IPMC. As expected, when the probe is positioned far from the surface, both tip–surface separation effects associated with membrane deformation and local ion pairing effects on the SECM current become negligible. Notably, for Pd-IPMC, the sinusoidal current response decays to nearly zero at a probe–surface separation of ~ 16 μm , whereas for Pt-IPMC a substantial response (~ 92 pA) is still observed at a separation of ~ 43 μm . This difference indicates a smaller effective swelling/contraction amplitude in

Pd-IPMC, consistent with its higher mechanical stiffness arising from Pd particle dispersion within the membrane (figures 3 and 4(b)) and its reduced bending actuation compared to Pt-IPMC (figure S4). The observed increase and subsequent decrease in response amplitude with probe–surface separation reflect three regimes: (i) a near-surface regime where ion pairing effects and tip-surface separation effects from electromechanical deformation both contribute, (ii) an intermediate-separation regime dominated by electromechanically induced membrane deformation, and (iii) a far-field regime where neither ion pairing nor deformation-related effects significantly influence the SECM response.

Although the present study demonstrates the capability of SECM to probe localized electrochemical responses in IPMCs under external electrical excitation, several important factors and limitations should be considered. As shown in the present study, the SECM responses are highly sensitive to probe–surface separation, particularly near the membrane surface, making it difficult to isolate local electrochemical information from electromechanically induced deformation effects. Future studies combining SECM with localized deformation measurement techniques such as atomic force microscopy (AFM) may help decouple electromechanical and electrochemical contributions and enable more quantitative investigation of local ion transport phenomena. In addition, the measured responses are influenced by surface morphology and the chemical environment in the chamber, requiring appropriate choices of UME diameter, surface preparation, and redox mediator. Furthermore, because the IPMC samples were fixed within epoxy resin during SECM measurements, mechanical constraints imposed by the resin may influence ion migration and electromechanical behavior. Therefore, development of customized operando SECM systems allowing unconstrained IPMC deformation during measurement would be valuable for future studies.

4. Conclusions

- This work investigates local electrochemical activities in Pt- and Pd-IPMCs under external electrical excitation using SECM.
- The fabricated Pt-IPMC and Pd-IPMC exhibited markedly different mechanical, electrical, electrochemical, and electromechanical behaviors.
 - Pd-IPMC contained Pd particles dispersed throughout the Nafion™ membrane, which contribute to increased mechanical stiffness.
 - Pd-IPMC also exhibited higher surface electrode resistance and lower capacitance, resulting in reduced bending actuation.
- SECM area-scan measurements under sinusoidal excitation detected current responses associated with membrane shrinkage caused by lithium cation diffusion from the membrane into the surrounding solution.
- Under DC bias, SECM responses were dominated by electron redistribution within the electrode domains rather than by cation concentration variations within the membrane.
 - Delayed current recovery after DC bias removal indicated slow cation redistribution from the electrode–membrane interface.
- Under square-wave excitation, current recovery occurred without measurable delay, consistent with the continuous electrode polarity alternation preventing long-lived polarization.
- Chronoamperometry under low-frequency sinusoidal excitation further revealed that:
 - SECM current responses reflect electromechanically induced membrane deformation.
 - Additional modulation at small probe–surface separations is associated with local cation concentration-related electrochemical effects such as cation association with the redox mediator.
 - Pd-IPMC showed weaker membrane deformation-related responses than Pt-IPMC, consistent with its higher membrane stiffness.
- Overall, this work demonstrates the capability of SECM to probe coupled electromechanical deformation and local electrochemical phenomena in IPMCs under external electrical excitation, providing spatially resolved electrochemical information that is difficult to obtain using conventional bulk characterization methods. By spatially resolving electrode and membrane domain responses, this work provides a methodological basis for future microscale SECM studies of electroactive polymers.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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