Redox-mediated proton transport of two-dimensional polyaniline-based nanochannels for fast capacitive performance

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Abstract

Two-dimensional (2D) materials are being increasingly exploited for ion transport and storage under nanoconfinement. Here we demonstrate distinct ion transport behavior upon potential-induced redox reaction in 2D tungstate anion cross-linked polyaniline (TALP) electrode. It is found that, in the neutral electrolyte, SO4^{2-} ion serves as the main charge carrier in 2D polyaniline backbone when the electrical double layer charging dominates. While in an acidic electrolyte, proton transport in TALP turns to be the dominant ion behavior that is associated with the proton-promoting surface redox processes. Moreover, higher capacitance along with better capacitive retention at a high rate is also demonstrated for TALP electrode in acidic electrolyte compared with that in the neutral environment. The results show that 2D nanoionics can be manipulated by applying redox-active materials to build the nanochannels that allow the regulation of surface charge and chemistry with potential-specific redox reactions.

KEYWORDS

ion behavior, nanofluidics, polyaniline, supercapacitors, two-dimensional materials

1 | INTRODUCTION

Nanofluidics has attracted increasing interest as an emerging area regarding fluid and ion transport confined at a nanometer scale.1–3 Some unique phenomena, such as ion-current rectification, fast water flow, and asymmetric ion transport, have been unveiled within nanofluidic channels, benefiting from the high surface-to-volume ratio, unscreened surface charge, overlapping electric double layer (EDL), and surface functionalization.4–6 The ion dynamics are normally correlated with the intrinsic geometry (channel shape, size, etc.)7–9 and surface properties (chemistry and charge density)10,11 of nanofluidic channels. Notably, external fields (electric, optical, or thermal) can be applied to regulate the ion and fluid transport behaviors within nanofluidic channels.1,12

Two-dimensional (2D) nanofluidic materials featuring well-organized flat nanochannels, adjustable structural and chemical properties have emerged as promising candidates for energy storage,13,14 and more importantly, established a precise platform for ion transport study.1,3,12 For example, Li et al.15 reported controlling ion
permeability in sub-2 nm graphene nanochannels by applying electrostatic biases to adjust the charge potential profile of EDL overlapping. Besides, Bo et al.15 observed that the dominant charge carriers in charged 2D graphene channels are governed by the respective diffusion coefficients for anions and cations. Ionic behavior in 2D nanofluidic channels is also sensitive to surface chemical properties. For instance, surface functionalization could tune ion selectivity in 2D graphene oxide membranes, such as cation/anion selectivity17 and selective transport of divalent cations (e.g., Co2+).10

It is noteworthy that external potential could induce surface Faradaic reactions when the 2D nanofluidic materials are redox-active, which leads to different surface chemical valence states.18 However, the impact of redox reaction on ionic behavior of Faradaic nanochannels is less discussed compared to the non-Faradaic graphene-based nanofluidic channels, despite the intense pursuing of Faradaic materials for electrochemical energy storage.18–20 Actually, ion dynamics in Faradaic nanofluidic channels can be more complicated because of their correlation with multiparameters (material, electrolyte, voltage, etc.). Zhang et al.21 revealed that the OH− intercalation on 2D MnO2 electrode in alkaline NaOH solution switched to Na+ adsorption and intercalation in neutral Na2SO4 electrolyte, which are attributable to the different adsorption energies of Na+ and OH− ions with [MnO6] octahedron. In contrast, significant capacitance gain for MXene electrodes was achieved with the acidic electrolyte rather than neutral electrolytes, which relates to the proton-intercalation pseudocapacitance.22 Nevertheless, little is known about the 2D ion behavior of conductive polymers, which represent another large class of electrode materials.23–25

A 2D polyaniline using tungstate as structural pillars and linkers (tungstate anion linked polyaniline [TALP]) demonstrated electrode processes that are switchable between non-Faradaic and Faradaic when the electrode potentials in neutral electrolytes are tuned.26,27 But the non-Faradaic and Faradaic ion behavior of the 2D TALP in different electrolytes are not known yet. In this study, we report the rapid Faradaic proton transport in the 2D TALP nanofluidic channels in the acidic electrolyte, which unlocks superior electrode performances compared with the non-Faradaic anion intercalation in the neutral electrolyte. The chemical state change of TALP electrode in acidic electrolyte is validated by means of X-ray photoelectron spectrometer (XPS), Raman spectroscopy, and colorimetric observation. Electrochemical quartz crystal microbalance (EQCM) is employed for information about the ion fluxes28,29 in TALP electrodes during both Faradaic and non-Faradaic processes. Our work suggests the promises of 2D conductive polymers with self-adaptive ionic behaviors for uses in electrodes for energy storage devices and other chemical processes (ion selection, separation, desalination, etc.) where mass transport is key.

2 | MATERIAL AND METHODS

2.1 | Synthesis of TALP

TALP powder was prepared using a method previously reported.26,27 Briefly, a solution containing 0.2 M H2SO4 and 0.2 M aniline was mixed with another 50 ml solution with 2.5 g ammonium metatungstate and 3.42 g ammonium persulfate. The obtained mixture was kept at 5°C for 24 h under continuous stirring, followed by filtration and washing with deionized water and ethanol. The yield solid was dried in a vacuum oven at 60°C overnight to get TALP powder. All the chemicals were purchased from Sigma–Aldrich and used without any further purification.

2.2 | Morphological and structural characterization

Morphological features were characterized by scanning electron microscopy (SEM; FEI Nova NanoSEM 450), and atomic force microscopy (AFM; Bruker Dimension ICON scanning probe microscope). X-ray diffraction (XRD) tests were performed using powder XRD (PANalytical Xpert X-ray diffractometer [Cu–Kα irradiation source, λ = 1.54056 Å] for TALP and polyaniline powder and Thin-film XRD (Bruker D8 Thin-Film XRD with rotating anode) for TALP electrodes. Structure features were also tested by XPS (Thermo ESCALAB250Xi) and Raman spectroscopy (Renishaw Raman microscope with 514 nm laser).

2.3 | Electrochemical measurement

Electrochemical performance of TALP was evaluated in a three-electrode system, where Ag/AgCl (saturated KCl) electrode serves as reference electrode and the activated carbon pallet works as the counter electrode. Working electrodes were prepared by pressing the mixture of TALP powder and carbon black (weight ration 9:1) onto stainless steel mesh in a round mould at a pressure of 7.6 t cm−2. Cyclic voltammograms (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance
spectroscopy (EIS) were conducted on a Biologic VSP potentiostat. A volume of 0.5 M H₂SO₄ and 0.5 M Li₂SO₄ were used as acidic and neutral electrolytes, respectively, where −0.2–0.8 V and −0.2–0.4 V were applied accordingly. EIS in both electrolytes was tested in the range of 20 mHz–200 kHz at open circuit potential.

2.4 | EQCM measurement

EQCM tests were performed with a CH instruments model CHI440C EQCM, where 7.995 MHz gold-coated AT-cut quartz crystal electrodes were used. A slurry solution was prepared by dispersing TALP, carbon black, and Nafion at a weight ratio of 8:1:1 in a mixture of water and ethanol solvent under sonication, which was then air-sprayed on the gold-coated area of quartz crystal (0.205 cm²) to make a working electrode. The coated quartz crystal was dried in a vacuum oven at 80°C overnight before any test. Platinum wire electrode and a custom-made Ag/AgCl electrode were used as counter and reference electrodes, respectively. Sauerbrey equation was used to translate frequency change into mass change on the electrode surface, \( \Delta f = -C_f \Delta m \), where \( C_f \) is the calibration constant. One Hertz frequency change is calculated to be 1.4 ng mass change in this testing system. Thin coating with a mass loading of around 10 µg cm⁻² was employed to minimize viscoelastic effects on frequency measurements. Additionally, the change in resonance resistance (ΔR), which is associated with the dissipation factor, was measured to examine the quality of EQCM data. Small ΔR change of quartz crystal (Figure S3) ensures that the validity of the Sauerbrey equation. The moles of water molecules \( (N_W) \) coinserted (coextracted) from TALP interspace is calculated by the following equation: \( N_W = (M_{\text{exper}} - M_{\text{Faraday}})/M_W \), where \( M_{\text{exper}} \) and \( M_{\text{Faraday}} \) refer to the experimental and theoretical molar mass of moving species for one net charge accumulated, respectively, \( M_W \) is the molar mass of water.

3 | RESULTS AND DISCUSSION

Two-dimensional TALP was synthesized following the procedure sketched in Figure 1A. With polyaniline chains as the conductive backbone, tungstate anions serve as linkers by forming multiple hydrogen bonds

![Image](https://via.placeholder.com/150)

**FIGURE 1** (A) Scheme of preparation process of TALP. (B) X-ray diffraction profile of TALP. (C) Scanning electron microscopy image of TALP sheets. (D) Atomic force microscopy image of TALP sheets directly grown on Si wafer with a height profile of selected sheets plotted in the inset. TALP, tungstate anion linked polyaniline
with polyaniline. The morphological and structural features of TALP sheets are characterized by SEM, AFM, and XRD. As presented in Figure 1B, the synthesized TALP powder exhibits one sharp main peak centered at $2\theta = 7.51^\circ$, representing the typical (001) peak with a large lamellar period of 11.76 Å. The typical layered structure feature of TALP is evidenced in the SEM image (Figure 1C), where a distinct stacked layered morphology is presented. Furthermore, AFM is conducted to characterize the feature of isolated TALP sheets directly grown on Si wafer, where typical 2D sheets with a thickness of around 4.0 nm are displayed in Figure 1D.

The 2D nanofluidic channels in TALP was previously utilized in various neutral metal sulfate solutions, which serve as fast ion transport paths to accommodate ion intercalation/deintercalation during charging and discharging. The redox activity of TALP is suppressed in those neutral electrolytes, as evidenced by the ex situ XPS results of electrodes under different potentials and the nearly rectangular CV curve. Considering that a low pH environment facilitates the redox activity in polyaniline, we wonder if TALP with polyaniline as the backbone will behave redox active when the electrolyte is switched from neutral to acidic. More importantly, the ion behavior change upon the redox process is monitored and discussed along with corresponding electrochemical performance.

The redox feature of TALP in 0.5 M H$_2$SO$_4$ electrolyte is evident in the CV curves (Figure 2A). Unlike the nearly rectangular CV curve of TALP in neutral electrolyte, three pairs of distinct redox peaks can be observed in the CV profile of TALP at 5 mV s$^{-1}$ (Figure 2A), indicating promoted redox reactions in the acidic electrolyte. The peak potentials and other features (three redox pairs, lower cathodic current than anodic one for Ox1/Re1, etc.) resemble those for polyaniline. The first pair of redox peaks (Ox1/Re1) arises from the transformation between completely reduced leucoemeraldine form and intermediate emeraldine form. Noticeable minor intensity for peak Re1 compared to that for Ox1 is attributed to the inferior electronic conductivity of leucoemeraldine. The redox pair Ox3/Re3 over 0.7 V at a low scan rate is attributed to the second stage oxidation of emeraldine to fully oxidized

![Figure 2](image-url)

**Figure 2** (A) Cyclic voltammetry curves of TALP electrode (mass loading, 5 mg cm$^{-2}$) at different scan rates in 0.5 M H$_2$SO$_4$. (B) The population of nitrogen groups derived from the ex situ XPS N1s spectra and (C) Raman spectra after holding TALP electrodes at corresponding potentials ($-200, 500, 800$ mV) for 1 h in 0.5 M H$_2$SO$_4$. (D) Optical images of TALP film grown on stainless steel taken at different potentials ($-200, 500, 800$ mV) in 0.5 M H$_2$SO$_4$. TALP, tungstate anion linked polyaniline
permigraniline. The Ox2/Re2 pair is most likely related to the redox reaction of hydrolysis products, which are usually identified as benzo/hydroquinone and p-aminophenol/benzoquinone imine redox couples. Implied by the redox characteristics observed from the CV profile, one may expect a chemical state change of the polyaniline chain of TALP to occur during the charging and discharging process. To reveal the redox state of the TALP electrode charged/discharged in an acidic electrolyte, ex situ XPS and Raman spectroscopy were employed. The N1s spectra (Figure S1) of TALP electrodes are deconvoluted to three peaks centered at 398.6, 399.9, and 401.5 eV, corresponding to imine (−N=), amine (−NH−) and protonated nitrogen (N+), respectively. The population of different nitrogen groups is compared in Figure 2B. With the increase of potential from −200 to 800 mV, an obvious tendency of less amine and more imine species is observed, indicating the transition from reduced unit to oxidized unit. Additionally, protonated nitrogen exists at all potentials with a small rise at higher potentials. Given that C–H bending vibration between 1100 and 1210 cm⁻¹ (in Raman spectra) is susceptible to the oxidation level of the polyaniline chain, we conducted Raman analyses for samples hold under different potentials (Figure 2C). For the lowest potential −200 mV, the C–H bending vibration is centered at 1185 cm⁻¹, corresponding to the leucoemeraldine base or salt. As protonated nitrogen is observed in the XPS result, the leucoemeraldine salt (LS) is believed to represent the main chemical state of the polyaniline chain in the TALP electrode at −200 mV. As the potential rises to 500 mV, the peak at 1171 cm⁻¹ emerges and maintains at 800 mV, which correlates with the C–H vibration of quinoid rings. Based on the peak evolution of C–H vibration, the nitrogen group of TALP electrodes proves oxidized at a higher potential.

TALP also demonstrated significant electrochromism as the bias changed, a well-known electrochromic behavior for polyaniline as a response to the redox reactions. The TALP thin film grown on stainless steel showed a distinct color change from light yellow at −200 mV to emerald green at 500 mV and finally turquoise blue at 800 mV, as presented in Figure 2D. Combined with XPS and Raman results, TALP electrode would transit from leucoemeraldine salt (light yellow) at −200 mV to emeraldine salt (emerald green) at around 500 mV, and eventually to the oxidized high-imine-proportion form (turquoise blue) at 800 mV, demonstrating the chemical state change in acidic electrolyte.

To reveal the effect of redox reaction on ion transport in 2D TALP channels, we further conducted EQCM tests for TALP in acidic and neutral electrolytes with the same sulfate anion (H₂SO₄ and Li₂SO₄). The mass loading of around 10 µg cm⁻² was used for EQCM electrodes, which showed small resistance changes ΔR during the full CV cycles in both electrolytes (Figure S3). The CV curves are distinguished in the two media (Figure 3A,B). In the H₂SO₄ electrolyte, the typical CV curve with three pairs of redox peaks is observed (dashed lines in Figure 3A). In neutral Li₂SO₄ electrolyte, TALP exhibits a nearly rectangular CV curve with a hump (dashed lines in Figure 3B). The applied narrow potential window is to avoid rigorous nonelectrostatic processes in the neutral electrolyte. Furthermore, the dependence of mass variations in these two electrolytes on electrode potential differs (solid lines in Figure 3A,B), which directly relates to their dominant current response (non-Faradaic or Faradaic). Basically, upon charging, the mass variations first rise with potential (Region I in both electrolytes), which start to decrease when the oxidation potentials are reached (the charging segments of Region II to IV in H₂SO₄ and Region II in Li₂SO₄). Mass change hysteresis is also noticed in both electrolytes, especially in the redox regions. Mass variations were measured in H₂SO₄ in a narrower potential region to restrict the redox reactions only for the first stage oxidation, where the same trend was observed (Figure S4). The observed hysteresis between anodic and cathodic cycles should be irrelevant to the hydrolysis products and may indicate kinetics difference of ion (de)intercalation induced by redox reactions. As the observed mass variation originates from the ion transport and exchange, it is reasonable to postulate that the pH-related Faradaic process could affect the ion dynamics in TALP.

During positive polarization, the possible ion behavior of the TALP electrode could be anion intercalation or cation deintercalation or ion exchange. Upon charging, when the non-Faradaic current dominates, the mass variation increases with potential (Region I in both electrolytes), which is most likely a result of the electrostatic adsorption of sulfate anions. In Li₂SO₄, the TALP electrode behaves mostly analogous to graphene-based electrodes, when the electrostatic process dominates the ion transport (referring to anion ingress/egress) in 2D TALP nanochannels. Calculated from the linear part of mass versus charge plot in Li₂SO₄ (Figure 3D), approximately 0.31 water molecules accompanied with sulfate ion intake for one net charge stored. The mass change pattern measured solely in non-Faradaic potential range (Figure S5) further verified the dominant anion process in Li₂SO₄ (Region I in Figure 3B,D), which is unlikely affected by the subsequent redox reactions.

With pronounced redox peaks, the impact of the Faradaic process on ion behavior is emphasized in
H₂SO₄. Three mass variation segments upon charging are subdivided based on the multiple oxidation stages. Correlating to the XPS results in Figure 2B, Region II and IV in Figure 3A refer to the oxidation from protonated leucoemeraldine to protonated emeraldine, and further to pernigraniline form, respectively. Mass variations decrease in those two regions, which should be attributed to the co-ion (H⁺) egress along with the oxidation from –NH– to –N= species. Linear changes of mass versus charge are also observed in those two regions (Figure 3C). The molar mass of transported species per net charge is calculated to be 22.81 (Region II) and 19.26 (Region IV) g mol⁻¹, quite close to the molar mass of H₃O⁺ (19 g mol⁻¹). In the corresponding discharging segments of Region V and VII, the mass variations increase due to dominated hydronium ion intake. Thus, these results indicate that proton (de)intercalation becomes the dominant ion behavior when redox reactions are involved. Besides, a similar mass variation trend is expected in Region III and VI since the redox reactions of the soluble hydrolysis products are also accompanied by proton involvement. However, different mass variation patterns are presented in the two regions. The mass variation increase observed in Region III and drop in Region VI should relate to the better solubility of reduced product over the oxidized one. Overall, based on EQCM results, it is deduced that ion intercalation in 2D TALP nanofluidic channels is governed by the Faradaic process, which drives a switch from sulfate ion transport to proton intercalation.

In response to the ion intercalation/deintercalation in 2D TALP channels, the structural evolution regarding phase change and interlayer space variation is concerned. Ex situ XRD tests were therefore conducted for TALP pellet electrodes (90% TALP/10% carbon black, 5 mg cm⁻²) holding at different potentials (Figure S6). Without new peaks emerging in the XRD pattern, no phase change should occur under applied potentials. Meanwhile, a shift in the (001) peak position indicates a c-lattice change in two electrolytes.

The interlayer spacing of a 2D electrode would change upon spontaneous ion (and/or water) insertion after immersing in electrolyte and bias-driven ion intercalation. As for the MXene electrode, Lukatskaya et al. reported that c-lattice parameter change could reach 5.1 Å after placing it in a potassium hydroxide solution. Even with only 1.0 Å expansion upon immersion, cycling of a MXene electrode in MgSO₄ could also result in a pronounced c-value change (9.6–10.1 Å) compared to the initial value. In 1T phase MoS₂, with an interplanar spacing of 6.15 Å for dry sample, an expansion of 6.63 Å could be reached for the cycled electrode in Li₂SO₄. In contrast, the interlayer expansion of immersed TALP electrodes is merely 0.17 Å in Li₂SO₄ and negligibly 0.05 Å in H₂SO₄. After applying potential, a further shift

![Figure 3](image-url)
of the (001) peak is also small (Figure S6a,b). For negative polarization in H₂SO₄ and Li₂SO₄, TALP electrodes exhibit expansions of ~0.63 and ~0.98 Å, corresponding to only 5.4% and 8.3% of the original spacing, respectively. The observed expansion should stem from the balance between steric effect and electrostatic attraction within anions and positively charged TALP sheets. A slight shrinkage compared to basal spacing is noticed for the TALP electrode polarized at 800 mV in H₂SO₄, which should be owing to the excess dehydration of interlayer galleries along with the continuous ion loss during charging. Given the small fluctuations of c-lattice, the 2D TALP electrode shows the suitability to accommodate various intercalants, which is favorable for applications valuing material integrity upon intercalation.

To gain further insight into the impact of the Faradaic process, we analyzed and evaluated the electrochemical features of the TALP electrode. The current response in CV scans (Figure 2A) is first integrated into the power-law relationship of current and scan rate ($i = av^b$) (as presented in Figure 4A,B). The $b$-value ranging from 0.79 to 1 suggesting a capacitive-dominated behavior in layer-structured TALP, instead of the sluggish diffusion-controlled intercalation process observed in traditional Li-ion batteries. In addition, the current response at different potentials is divided into two parts, capacitive and diffusion current. The 73.4% of total capacitance response is contributed by the capacitive process at a scan rate of 5 mV s⁻¹, which increases with scan rate and scores 87.4% at 50 mV s⁻¹ as shown in Figure 4C,D. Combined, with the incorporation of Faradaic reactions, the TALP electrode still features dominantly fast capacitive features like what was recognized in various neutral media.

Galvanostatic charge–discharge (GCD) curves of TALP electrode are also provided at various current densities to evaluate the capacitance performance (Figure 5A,B). The nearly linear profile with several

![Figure 4](image-url)
inflexion points in Figure 5A is consistent with the pseudocapacitive feature as observed in CV curves (Figure 2A). A capacitance loss is recognized during the 10 cycles tested at low current density, 0.5 A g\(^{-1}\) (Figure 5B) in H\(_2\)SO\(_4\), where a similar deterioration is not seen in Li\(_2\)SO\(_4\). This phenomenon directly relates to polyaniline degradation, which occurs at the high potential region and is an acid-catalyzed reaction.\(^{33,35}\)

Higher capacitances are nevertheless exhibited in H\(_2\)SO\(_4\) electrolyte at all tested current densities on account of the extra charge from the Faradaic processes (as shown in Figure 5B).

In addition, TALP electrode shows superior rate performance in H\(_2\)SO\(_4\), which is pursued in electrode materials for fast charging/discharging capability.\(^{18,24}\) Based on their capacitances at 0.5 A g\(^{-1}\), 50.4% capacitance retention can be achieved in H\(_2\)SO\(_4\) after increasing the current density to 20 A g\(^{-1}\), while merely 22.9% of the capacitance is retained at 5 A g\(^{-1}\) in Li\(_2\)SO\(_4\). This enhancement presumably benefits from the dominant transport of protons in H\(_2\)SO\(_4\), whose higher mobility compared to sulfate ions\(^{44}\) could contribute to efficient charge storage at a high rate. Thus, except for the normally recognized higher capacitance, the incorporated redox reactions could also result in better rate capability in the 2D TALP electrode.

To confirm the fast proton transport, the electrochemical impedance spectrum (EIS) is conducted for TALP electrodes in H\(_2\)SO\(_4\) and Li\(_2\)SO\(_4\) (Figure 5C). The same characteristic is observed in both electrolytes, with a single semicircle in the high-frequency region and a straight line in the low-frequency region. Accordingly, the equivalent circuit consisting of electrolyte resistance (R\(_s\)), constant phase element (CPE), charge transport resistance (R\(_ct\)), and Warburg diffusion element (W) is used for the fitting of Nyquist plots. As displayed in Table 1, major differences are in R\(_s\), R\(_ct\), and W values, suggesting the different ion and charge transport environments produced by these two electrolytes. Specifically, values of R\(_s\) and R\(_ct\) in H\(_2\)SO\(_4\) electrolyte are almost

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**Figure 5**

(A) Galvanostatic charge–discharge curves of TALP electrode (mass loading, 5 mg cm\(^{-2}\)) at various current densities in 0.5 M H\(_2\)SO\(_4\). Volumetric capacitance at different current densities (B) and Nyquist plot (C) tested in 0.5 M H\(_2\)SO\(_4\) and 0.5 M Li\(_2\)SO\(_4\) electrolyte (fitting data of Nyquist plot are shown as grey dashed line in the inset). (D) Comparison of volumetric capacitance for TALP and normal polyaniline electrodes with different mass loadings at 0.5 A g\(^{-1}\) tested in 0.5 M H\(_2\)SO\(_4\). TALP, tungstate anion linked polyaniline
half of those in Li2SO4 electrolyte, indicating less electrolyte resistance and facile charge transfer in the acidic environment. Moreover, a much lower Warburg coefficient is observed in the H2SO4 electrolyte compared to that in the Li2SO4 electrolyte, revealing effective ion diffusion in the acidic environment. Bode plots in two electrolytes are also provided for frequency-dependent parameters (Figure S9). The higher real capacitance value at low frequencies in H2SO4 compared to that in Li2SO4 (Figure S9a) is consistent with the results from GCD measurements (Figure 5B). Furthermore, the relaxation time constant $\tau_0$ for TALP electrodes in two electrolytes can be deduced from the peak frequencies $f_0$ of imaginary capacitance (Figure S9b). The calculated relaxation time constant ($\tau_0 = 1/2\pi f_0$) in H2SO4 and Li2SO4 is 1.55 and 2.49 s, respectively, which indicates the improved rate capability in H2SO4. Combined, proton abundant H2SO4 electrolyte provides TALP electrode with a fast and effective charge and mass transport environment.

Thickness-dependent capacitance has always been a challenge for practical application due to long-distance and sluggish electron/ion transport in required thick electrodes.18 It was reported for 2D MoS2 that obvious capacitance reduction (around 20%), as well as narrower potential window, are observed when the electrode thickness rises from 1 to 5 μm.22 MXene electrodes even lose more than 50% of the volumetric capacitance when increasing electrode thickness from 5 to 75 μm.22 Previously, we have shown limited volumetric capacitance loss for TALP electrodes with mass loading of 10 and 20 mg cm$^{-2}$ in neutral electrolytes by virtue of interlayer water.27 In this case, the favorable feature of thick TALP electrodes is expected to be reserved in acidic electrolytes with larger capacitance. Thick TALP electrodes with higher mass loading are thus tested in H2SO4. As presented in Figure 5D, over 90% of the capacitance can be retained when increasing TALP electrode mass loading from 5 to 20 mg cm$^{-2}$ (thickness: ~30–110 μm). To further reveal the facile ion transport in 2D TALP nanofluidic channels, a comparison is also provided by using normal polyaniline electrodes (XRD pattern provided in Figure S10) with the same mass loadings, which show only 69% retention in the thick electrode (Figure 5D). The capacitance of polyaniline electrode only exceeds that for TALP electrode at a mass loading of 5 mg cm$^{-2}$, which should be attributed to the high portion of accessible electrochemical-active sites at low mass loading and low current density as the capacitance decays fast as current density increases (Figure S11). Consequently, 2D TALP nanofluidic channel demonstrates its capability of effective proton transport in thick electrode.

### Table 1

| Electrolyte | CPE | Rct (Ω) | W |
|-------------|-----|---------|---|
| H2SO4       | 0.292 | 0.417 × 10$^{-3}$ | 0.796 | 2.248 | 3.68 |
| Li2SO4      | 0.518 | 0.402 × 10$^{-3}$ | 0.727 | 3.913 | 8.417 |

### 4 CONCLUSION

In summary, we have shown redox-mediated ion transport behavior in 2D polyaniline-based material, of which the correlation with electrochemical performance is discussed. With the introduction of Faradaic processes in the 2D TALP system, the ion transport pattern would switch from an anion-dominated process to predominant proton transport mode. Meanwhile, except for extra charge contribution, the additive protons also serve as fast and effective charge carriers in 2D TALP nanofluidic channels, resulting in high capacitance retention at a high rate and for thick electrodes. Beyond correlating ion transport behavior with electrochemical performance, this study also paves the way for understanding ionic response in 2D confined systems consisting of both physical (electrostatic interaction) and chemical (redox state) modulations.

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### CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

### DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of the article at the publisher's website.

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