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# Aqueous Multivalent Charge Storage Mechanism in Aromatic Diamine Based Organic Electrodes

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## Abstract

Rechargeable batteries employing aqueous electrolytes are more reliable and cost effective as well as possess high ionic conductivity compared to the flammable organic electrolyte solutions. Among these type of batteries, aqueous batteries with multivalent ions attract more attention in terms of providing high energy density. Herein, electrochemical behavior of an organic electrode based on highly aromatic polymer containing 2,3-diaminophenazine repeating unit, namely poly(ortho-phenylenediamine) (PoPD), is tested in two different multivalent ions ( $Zn^{2+}$  and  $Al^{3+}$ ) containing aqueous electrolytes, *i.e.*, in zinc sulfate and aluminum chloride solutions. PoPD is synthesized *via* electro-polymerization and its ion transport and storage mechanism are comprehensively investigated by structural and electrochemical analyses. The electrochemical quartz crystal microbalance (EQCM), time-dependent FTIR and EIS analyses as well as ex-situ XRD observations established that along with the  $Zn^{2+}$  or  $Al^{3+}$  ions, reversible proton insertion/extraction also takes place. Contrary to the most of the organic electrodes that requires the use of conductive carbon additives, electrodeposited PoPD electrode is intrinsically electrically conductive enough, resulting in a carbon-free electrode assembly. In addition, its discharge products do not dissolve in aqueous medium. As a whole, the resulting PoPD electrode delivers excellent rate performances with prolonged cycle life in which discharge capacity of  $\sim 110$  mAh  $g^{-1}$  in 0.25 M  $AlCl_3$  and

~93 mAh g<sup>-1</sup> in 1 M ZnSO<sub>4</sub> aqueous electrolyte after 1000 cycles at a current density of 5C have been achieved.

Keywords: aqueous electrolyte batteries, multivalent ions, organic electrodes, EQCM, electrode/electrolyte interface

## 1. Introduction

The 2000 Nobel Prize (Heeger, MacDiarmid and Shirakawa) in conductive polymers (CPs) persuades the academic and industrial community to turn their attention towards CPs owing to a vast domain of implementations ranging from electrochemical energy storage to bioelectronics or bio(chemical)sensors.<sup>1-2</sup> Considering the increasing energy consumption and the demand for the clean resources, rechargeable batteries are regarded as one of the most appealing alternatives.<sup>3</sup> Especially, aqueous rechargeable metal-ion batteries as electrochemical energy storage devices are promising due to their safety, low manufacturing cost, environmental benignity, nontoxicity and high ionic conductivity.<sup>4</sup> Moreover, multivalent-ion aqueous batteries including Al<sup>3+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> or Zn<sup>2+</sup> provide much higher volumetric energy density compared to the monovalent-ion counterparts.<sup>5</sup>

Among multivalent-ion aqueous rechargeable systems, zinc-ion battery (ZIBs) and aluminum-ion battery (AIBs) attract tremendous interest due to high theoretical volumetric capacities of aluminum (8034 mAh cm<sup>-3</sup>) and zinc (5857 mAh cm<sup>-3</sup>) originating from the multi-electron transfer during electrochemical process.<sup>6-8</sup> Moreover, aluminum is the third most abundant element in the Earth's crust, facilitating a more affordable manufacturing cost. On the other hand, from the active material utilization point of view, zinc possesses high theoretical capacity of 820 mAh g<sup>-1</sup> compared to other metal-ion batteries and high compatibility with aqueous electrolyte, which make zinc a promising anode material for ZIBs.<sup>4</sup> However, passivation layer on aluminum anode, hydrogen evolution and corrosion restrict the utilization of aluminum

metal in aqueous environment.<sup>9</sup> In order to overcome these problems, aluminum anode is preferred to be used with the combination of imidazolium salts and aluminum chloride (ionic liquid (IL)) electrolyte.<sup>10</sup> Among the class of organic electrode choices,<sup>11-12</sup> CPs such as polyaniline (PANI),<sup>13</sup> polypyrrole (PPy),<sup>14</sup> polythiophene (PTh), poly-(*p*-phenylene) (PPP) and poly(3,4-ethylenedioxythiophene) (PEDOT)<sup>15</sup> have commonly been used as electroactive materials in ZIBs as well as AIBs. Proposed redox mechanism for charge storage is based on the abundance of delocalized  $\pi$  electrons in CP which facilitate anions/cations insertion during discharge/charge process as well as high local proton storage ability of polymer backbones.<sup>16</sup> Although the electrochemical performance of CPs in ZIBs have been comprehensively investigated,<sup>12</sup> aluminum system is mostly studied in molten salt or in ionic liquids (ILs) containing  $\text{AlCl}_3$  and 1-ethyl-3-methylimidazolium (PPy,<sup>17</sup> polythiophene (PTh),<sup>18</sup> PANI,<sup>19</sup> poly-(*p*-phenylene) (PPP)<sup>20</sup>), only a few studies have shown the electrochemical activity of CPs in rechargeable aluminum-ion batteries in aqueous medium.<sup>21</sup>

Phenylenediamines (-orto, -meta, -para directed) including active amino and imino groups are classified as aromatic diamines.<sup>22</sup> Polymerization of phenylenediamine takes place *via* chemical and electrochemical oxidation process,<sup>23</sup> and obtained conductive polymers have been broadly utilized in multiple applications such as sensors,<sup>24</sup> supercapacitors,<sup>25</sup> anodes for Li-ion batteries in organic electrolytes.<sup>26</sup> Electrochemical performance of PoPD has also been evaluated in aqueous metal-ion batteries. *Sivakkumar et al.* synthesized PoPD on carbon electrode and tested in 1 M zinc sulfate (pH= 4) electrolyte in which a discharge capacity of 127 mAh g<sup>-1</sup> was achieved.<sup>27</sup> In a recent study, PoPD was employed as a positive electrode for zinc-ion aqueous battery in which C=N bond of phenazine unit was found to be responsible for zinc ion storage.<sup>28</sup>

As an extension to previous studies, herein, electrochemical performance of the electropolymerized PoPD electrodes was investigated in two different aqueous electrolytes containing zinc sulfate and aluminum chloride. Our aim is to clarify the nature of the ions ( $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$  or other ions included in the electrolyte) taking part in the charge compensation, as well as any other interfacial process that may intervene with

ions' interaction with the electrode material. To the best of our knowledge, this is the first report investigating both the performance and the storage mechanism of a conducting polymer electrode in aqueous  $\text{Al}^{3+}$  or  $\text{Zn}^{2+}$  containing electrolyte in a comparative manner. To elucidate the performance and the charge storage properties, cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS) were employed and complemented with time dependent FTIR and *ex-situ* XRD analyses to acquire compositional and structural information. Additionally, to reach a mechanistic understanding of the nature of the ions taking part in the charge storage, we have employed *in situ* Electrochemical Quartz Crystal Microbalance (EQCM) based methods.<sup>29-31</sup> *In-situ* EQCM and EQCM with motional resistance (EQCM-R) or dissipation monitoring (EQCM-D),<sup>32-36</sup> have been shown to be beneficial in the gravimetric,<sup>34, 36</sup> structural,<sup>37</sup> and viscoelastic property<sup>38</sup> analysis of energy storage materials. To perform such analyses, the PoPD electrodes were electrodeposited as thin layers on the conductive electrode of a quartz crystal resonator and were used as working electrodes. The frequency as well as motional resistance changes ( $\Delta f$  and  $\Delta R_m$ ) occurring in response to an electrochemical process (*e.g.*, insertion of  $\text{Zn}^{2+}$  or  $\text{Al}^{3+}$ ) at the electrode/electrolyte interface are concurrently monitored and interpreted in correlating with the other (electro)chemical results obtained.

## 2. Experimental Section

2.1 Preparation of PoPD Electrode: Electro-polymerization of oPD monomer was performed *via* CV, using a three-electrode configuration. In this latter, graphite plate was used as a working electrode ( $\sim 2 \text{ cm}^2$ ), a platinum wire as a counter electrode, and an Ag/AgCl (saturated 3.5 M KCl) was used as a reference electrode. Firstly, 1,2-diaminobenzene (oPD) monomer (Sigma-Aldrich) (5 mM) was dissolved in 0.1 M  $\text{H}_2\text{SO}_4$  solution and then, followed by electrodeposition on the graphite plate for 1000 polymerization cycles in a potential range from -0.4 V to 0.8 V *vs.* Ag/AgCl (saturated 3.5 M KCl) with a scan rate of  $50 \text{ mV s}^{-1}$ . Before and after electro-polymerization process, graphite plate was weighed to

determine the active mass of the PoPD electrode. The as synthesized PoPD electrode was used for the electrochemical tests without any further modification.

EQCM (Electrochemical Quartz Crystal Microbalance) measurements were carried out using AT-cut 9 MHz quartz resonators (AWS, Valencia, Spain) modified with gold electrodes as substrates. Electrochemical polymerization of oPD monomer (1,2-diaminobenzene) was carried out according to previously reported literature.<sup>39-40</sup> Briefly, 5 mM oPD was dissolved in 0.1 M H<sub>2</sub>SO<sub>4</sub> and cycled 200 times within the potential range of -0.4 V and 0.8 V *vs.* Ag/AgCl at a scan rate of 50 mV s<sup>-1</sup>. In order to keep the gravimetric regime of the microbalance, the number of cycles have been restricted to 200 (unlike the graphite surface) which gives sufficient coverage of PoPD film on the gold electrode (0.2 cm<sup>2</sup>) of the quartz resonator.

**2.2 Morphological and Compositional Characterization of PoPD Electrode:** Functional groups of PoPD were investigated using Fourier-transformed infrared (FTIR) (Perkin Elmer Spectrum 100). Scanning electron microscopy (SEM) (FEI PHILIPS, XL30 SFEG SEM) conjugated with Energy Dispersive X-Ray Spectroscopy (EDS) was employed to examine the surface morphology and elemental analysis of PoPD surface. X-Ray Diffraction patterns of PoPD and graphite were recorded by using X-Ray diffraction Bruker- D8 Advance Bruker AXS.

**2.3 Electrochemical Measurements on Zn/PoPD and Al/PoPD Cells:** Zn/PoPD cell was fabricated using PoPD electrode as cathode, Pt wire as counter electrode, Ag/AgCl (sat. 3.5 M KCl) as reference electrode and 1 M ZnSO<sub>4</sub> aqueous solution as electrolyte. Al/PoPD cell was tested with the same configuration with 0.25 M AlCl<sub>3</sub> aqueous solution as the electrolyte. The active mass loading of the PoPD electrode is 0.15 mg per cm<sup>2</sup> on graphite electrodes and it has been kept fixed for both the Zn and Al systems during electrochemical measurements. During the galvanostatic cycling, 1C current density corresponds to 496 mA g<sup>-1</sup> in Zn<sup>2+</sup> containing electrolyte and 744 mA g<sup>-1</sup> in Al<sup>3+</sup> containing electrolyte. The CV (at a scan rate of 1, 5 and 10 mV s<sup>-1</sup>) and the GCD tests were carried out in a potential range of -0.95 to 0.8 V *vs.* Ag/AgCl (sat. 3.5 M KCl) in three-electrode cell configuration for both Zn/PoPD and Al/PoPD

systems. Electrochemical impedance spectroscopy (EIS) was carried out at open circuit voltage (OCV), before and after 1000 cycles at a frequency range of 100 kHz to 1 mHz. All the electrochemical studies were carried out by Bio-Logic VMP3 potentiostat/galvanostat. The ionic conductivity and pH of different concentrations of aqueous electrolytes were measured by HANNA HI2315 conductivity meter and HANNA pH meter (egde HI2002-02), respectively.

EQCM measurements were carried out in 1 M ZnSO<sub>4</sub> and 0.25 M AlCl<sub>3</sub> aqueous solution in a three-electrode configuration using a Bio-Logic electrochemical workstation (Biologic SP200) coupled with a lab-made QCM device. As deposited PoPD films, platinum wire and Ag/AgCl electrode were used as the working, counter and reference electrodes, respectively. The EQCM with motional resistance monitoring were conducted by an Agilent 4294A impedance analyzer coupled with a Bio-Logic electrochemical workstation (Biologic SP200).

The mass variation ( $\Delta m$ ) can be derived from the frequency variation ( $\Delta f$ ) of the QCM using the Sauerbrey equation<sup>41</sup>: ( $\Delta f = -k_s \cdot \Delta m$ , where,  $k_s = 16.31 \times 10^7 \text{ Hz g}^{-1} \text{ cm}^2$ , is the experimental sensitivity coefficient). Then, the average mass per electron,  $MPE = \frac{n \cdot F \cdot \Delta m}{\Delta Q}$  ( $n$  is the number of electrons transferred), can be calculated which estimates the nature of the transferred species (anion, cation, water molecules) during cycling. The negative and positive signs of MPE (mass per electron) correspond to the cationic and anionic contributions, respectively.

### 3. Results and Discussions

**3.1 Electrode preparation and characterization:** Electro-polymerization of oPD monomer on graphite plate was performed in acidic environment using cyclic voltammetry. As shown in Figure 1a, during the electrodeposition of PoPD on graphite, intensity of irreversible anodic peak at 0.8 V was decreased gradually due to the decline in activity of monomer, owing to the freshly formed PoPD polymer.<sup>42</sup> However, the current of the cathodic and anodic peaks (at -0.17 V and -0.10 V, respectively) were increased progressively for the subsequent CV cycles, indicating the growth of PoPD. Electrochemical synthesis of

PoPD was limited to 1000 CV cycles for our study in order to inhibit the non-electroactive polymer films formed for the following cycles. *Malinauskas et al.* concluded that particular thickness of PoPD layer could be obtained *via* anodic electro-polymerization method owing to the low electrical conductivity of PoPD.<sup>43</sup> *Yano et al.* reported that the thickness of PoPD film on ITO electrode could not be more than 0.85  $\mu\text{m}$  corresponding 1000 CV cycles.<sup>44</sup> Consequently, common electro-polymerization process of oPD takes place in two steps: *i*) oPD monomer oxidizes to produce cation radical and *ii*) this radical is dimerized by coupling *via* C-N or C-C. After coupling, PoPD as ladder polymer bearing phenazine rings is successfully generated with oxidation of predominant head-to-tail structure dimers.<sup>42, 45</sup> Likewise, electro-polymerization of oPD using cyclic voltammetry in previous studies have also exhibited analogous redox behavior.<sup>40, 46</sup>

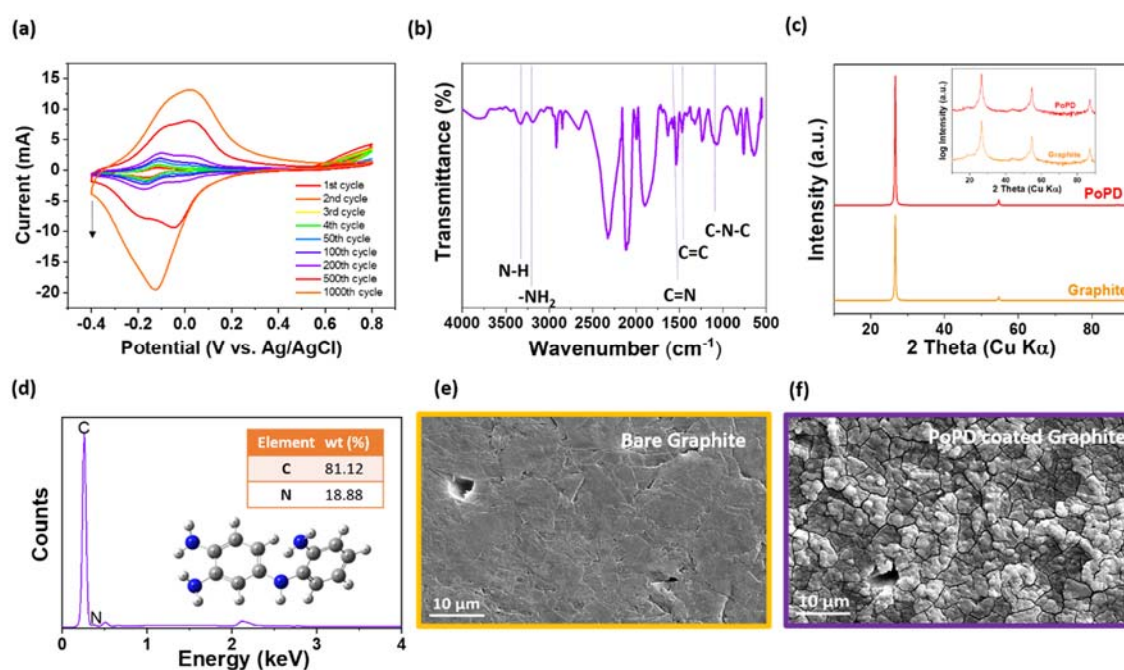


Figure 1: (a) CV curves during the electro-polymerization of oPD on graphite plate, (b) FTIR spectrum of PoPD electrode, (c) XRD patterns of graphite and PoPD electrode deposited on graphite plate, inset: XRD patterns of graphite and PoPD electrode with log intensities at the y-axis, (d) EDS analysis of PoPD electrode, inset image: proposed PoPD repeating unit, inserted from Figure S2, SEM images of (e) bare graphite plate and (f) PoPD electrode deposited on graphite plate.



Molecular structure of PoPD electrode was investigated by FTIR (Figure 1b). The representative peaks at 3324  $\text{cm}^{-1}$  and 3180  $\text{cm}^{-1}$  are ascribed to -NH- and -NH<sub>2</sub>, respectively. Peaks in the region between 1700 to 3000  $\text{cm}^{-1}$  attributed to atmospheric carbon dioxide<sup>47</sup> as well as those from the graphite substrate (Figure S1). Stretching of C=N and C=C vibrations were observed at the corresponding peaks at 1629  $\text{cm}^{-1}$  and 1534  $\text{cm}^{-1}$ , representing the successful electro-polymerization of oPD. The peak at 1075  $\text{cm}^{-1}$  was attributed to the C-N-C band. The bands between 972-759  $\text{cm}^{-1}$  were originated from wagging of C-H group (out-of-plane C-H bending), indicating the presence of aromatic benzene ring. Our findings are well consistent with the FTIR signature spectrum of electropolymerized PoPD film in the previous reports.<sup>23, 27, 42, 46, 48-49</sup>

X-ray diffraction pattern of graphite and PoPD electrode are shown in Figure 1c. Well-defined sharp peaks at 26.6°, 54.7° and 87.1° corresponds to (002), (004) and (112) planes of graphite.<sup>50</sup> However, diffraction peaks corresponding to PoPD could not be detected, revealing its amorphous structure. EDS elemental spectrum of PoPD electrode demonstrated the presence of carbon and nitrogen (Figure 1d). Then, we tried to rationalize the molecular structure of PoPD repeating unit by using density functional theory (DFT) method (B3LYP) with 6-31G (d) basis set.<sup>51</sup> Visualization was performed by Gaussian 09 program package. When we calculate the weight ratio according to the repeating units in the figure (Figure S2), for 1,4 substituted benzenoid-quinoid structure of PoPD, 79.13 % of C and 15.38 % of N were found. Thus, the weight ratio of C and N is in a good agreement with EDS elemental analysis (81.12 % for C and 18.88 % for N). Additionally, the penetration depth in EDS analyses is around few microns which then probes the C from the graphite substrate. Hence slightly more weight estimated for C can be assigned to the carbon originated from the graphite current collector. To the best of our knowledge, the real structure of PoPD is an open ring polymer with free amine groups. The open ring polymer structure that is estimated in Figure S2 is close to that demonstrated in the work of Samanta *et al.*<sup>52</sup> which has investigated the polymerization process of oPD monomer in H<sub>2</sub>SO<sub>4</sub> medium.

Turning to the morphological characterizations, comparing the SEM images of bare graphite (Figure 1e) and PoPD film coated graphite (Figure 1f), it can be concluded that bare graphite has smoother surface than that of covered with PoPD. Lumpy surface of PoPD confirms that it covers the surface of graphite plate uniformly after 1000 CV cycles during electro-polymerization process. These combined results attest the effective electro-polymerization of PoPD on the graphite plate.

### 3.2 Electrochemical characterization and performance tests of PoPD on graphite plates

Prior to the electrochemical tests, pH and ionic conductivity values were measured for both  $\text{AlCl}_3$  and  $\text{ZnSO}_4$  containing aqueous electrolytes. While the pH of the  $\text{AlCl}_3$  solution is rather acidic and it decreases from pH 3.2 to 0.5 by changing the concentration from 0.25 M to 3.0 M (Figure 2a), pH of the  $\text{ZnSO}_4$  solution ranges from 5.6 and 4.4 depending on the concentration of the  $\text{ZnSO}_4$  solution (Figure 2b). The ionic conductivity values of both electrolytes behave also differently. The ionic conductivity of  $\text{AlCl}_3$  solution is much higher than that of  $\text{ZnSO}_4$  and reaches a maximum value at 1.5 M  $\text{AlCl}_3$  concentration ( $187 \text{ mS cm}^{-1}$ ). The conductivity of  $\text{ZnSO}_4$  solution ranges from 18 to  $63 \text{ mS cm}^{-1}$  when the salt concentration rises from 0.5 M to 3.0 M. With the aim of keeping the ionic conductivity of the electrolytes as close as possible, all electrochemical characterizations have been carried out with 0.25 M  $\text{AlCl}_3$  (pH 3.34) and 1 M  $\text{ZnSO}_4$  (pH 5.16) aqueous solution with almost similar ionic conductivities of  $49.6 \text{ mS cm}^{-1}$  and  $50 \text{ mS cm}^{-1}$ , respectively (Figure 2a and b). Two metal salts with the same anion were not conceivable to eliminate the interference of anions on the charge storage mechanism of the PoPD electrode for several reasons. The  $\text{ZnCl}_2$  (anhydrous) was not favored because it forms zinc oxychlorides upon dissolution in water leading to a turbid solution and some precipitation.<sup>53</sup> Even though those precipitations can be simply eliminated by the use of a few drop of HCl addition, addition of acid solution changes the pH along with the entire charge storage mechanism due to the altered  $\text{Zn}^{2+}/\text{H}^+$  ratio in the electrolyte. Another point is the limitation of the EQCM measurement in a turbid solution (which would prevent the QCM working as a gravimetric probe, as discussed in Part 3.3). Therefore, a correlation

between the interface property and performance would not be possible in  $\text{ZnCl}_2$  solution. The reason why  $\text{Al}_2(\text{SO}_4)_3$  was not favored is related with (i) the extremely acidic nature of the resulting solution that causes damage on the substrates and (ii) its low ionic conductivity<sup>54</sup> that resulted in a very poor cycling performance (data now shown). Consequently, due to their superiority in different aspects,  $\text{AlCl}_3$  and  $\text{ZnSO}_4$  electrolytes were chosen as multivalent charge carriers to study the charge storage mechanism of the PoPD electrode, over  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{ZnCl}_2$  solutions.

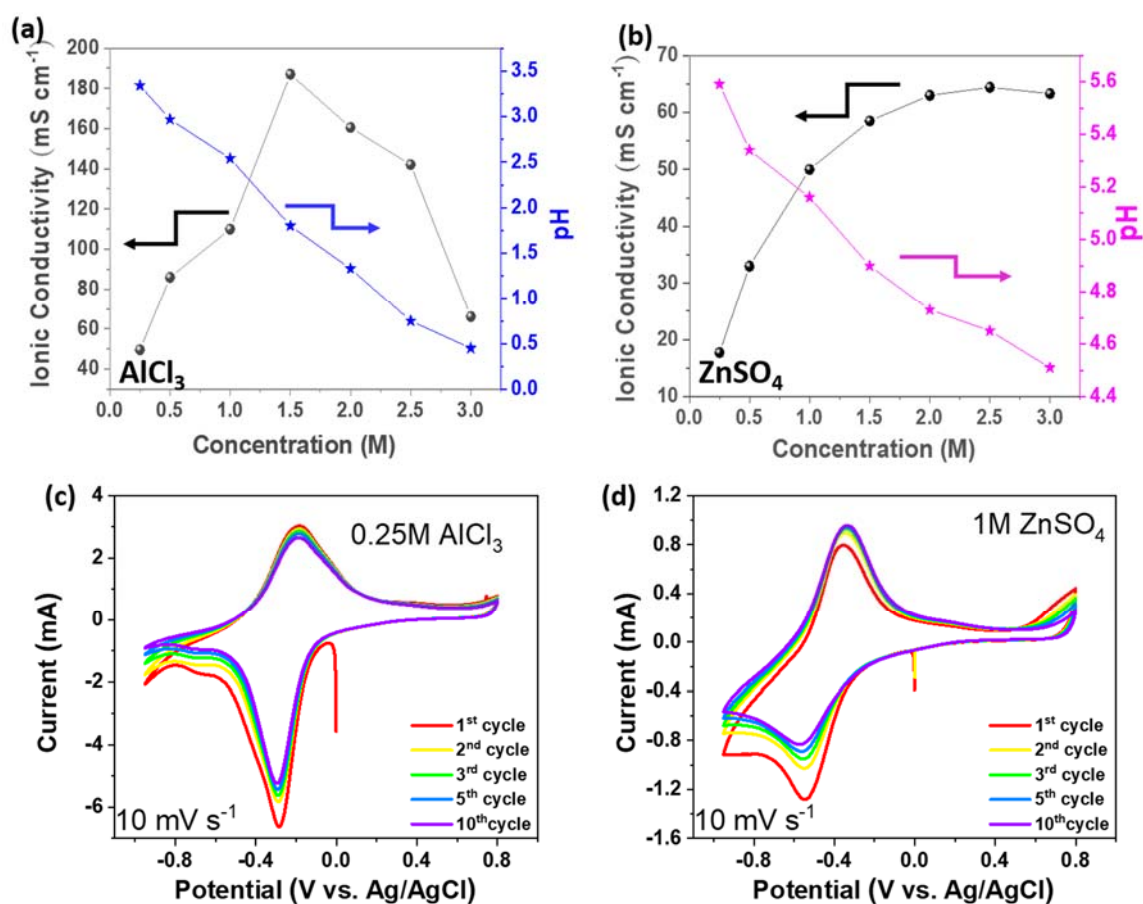


Figure 2: Ionic conductivity and pH of the different electrolyte concentration of (a)  $\text{AlCl}_3$  and (b)  $\text{ZnSO}_4$ . CV curves of PoPD on graphite electrodes at a scan rate of  $10 \text{ mV s}^{-1}$  in (c) 0.25 M  $\text{AlCl}_3$  electrolyte and in (d) 1 M  $\text{ZnSO}_4$  electrolyte.

To investigate the electrochemical behavior of PoPD, deposited on graphite plates, in the two different aqueous electrolytes, CV was initially carried out in 0.25 M  $\text{AlCl}_3$  and 1 M  $\text{ZnSO}_4$  at a scan rate of  $10 \text{ mV s}^{-1}$  between -0.95 and 0.8 V vs. Ag/AgCl. The CV curves of PoPD in aqueous  $\text{AlCl}_3$  electrolyte exhibit a

cathodic peak at -0.28 V and an anodic peak at -0.19 V during the first reduction and oxidation cycle, respectively. Throughout subsequent cycles, similar electrochemical response was observed, which can be attributed to a reversible and fast electrochemical process into/from PoPD electrode (Figure 2c). On the other hand, cyclic voltammograms of PoPD in 1 M ZnSO<sub>4</sub> aqueous solution exhibit one cathodic peak at -0.55 V and one anodic peak at -0.35 V (Figure 2d), which may signify insertion/extraction of ions into/from active side of PoPD electrode. The slight difference in the peak position of the redox couple obtained in Al<sup>3+</sup> and Zn<sup>2+</sup> containing electrolytes could be assigned to the different hydration radius and ionic hydration energies of the corresponding cations.<sup>55</sup>

The galvanostatic discharge/charge performance of PoPD electrode in aqueous electrolytes of 1 M ZnSO<sub>4</sub> and 0.25 M AlCl<sub>3</sub> has been investigated at different current densities in three-electrode configuration. As seen in Figures 3a and 3b, the discharge/charge profiles demonstrate an average voltage of around -0.40 V in 1 M ZnSO<sub>4</sub> and -0.20 V in 0.25 M AlCl<sub>3</sub>, which are in well agreement with the CV results. PoPD electrode in 1 M ZnSO<sub>4</sub> delivered average discharge capacities of around 32, 42, 58, 70 and 112 mAh g<sup>-1</sup> (Figure 3c), while in 0.25 M AlCl<sub>3</sub>, 213, 122, 127, 131 and 156 mAh g<sup>-1</sup> discharge capacities were obtained at the current densities of 20 C, 15 C, 10 C, 8 C and 5 C, respectively (Figure 3d), demonstrating that PoPD electrode exhibited a better rate performance in 0.25 M AlCl<sub>3</sub> electrolyte. Improved rate capability in AlCl<sub>3</sub> compared with its Zn counterpart and the reasons behind this dissimilar performance have further been probed with ion transport and interfacial ion transfer analyses with EIS and EQCM, respectively (Section 3.3). Moreover, the long-term cycling performance of PoPD was assessed at the same current density (5C) in both electrolytes. As depicted in Figure 3e, PoPD delivered an initial discharge capacity of 379 mAh g<sup>-1</sup> in 0.25 M AlCl<sub>3</sub> and after 1000 cycles a capacity of 110 mAh g<sup>-1</sup> was obtained with a capacity retention of 56 %. Figure 3f illustrates the cycling performance in 1 M ZnSO<sub>4</sub> that PoPD exhibited the first discharge capacity of 143 mAh g<sup>-1</sup> in 1 M ZnSO<sub>4</sub>, and retained its discharge capacity of 93 mAh g<sup>-1</sup> after 1000 cycles.

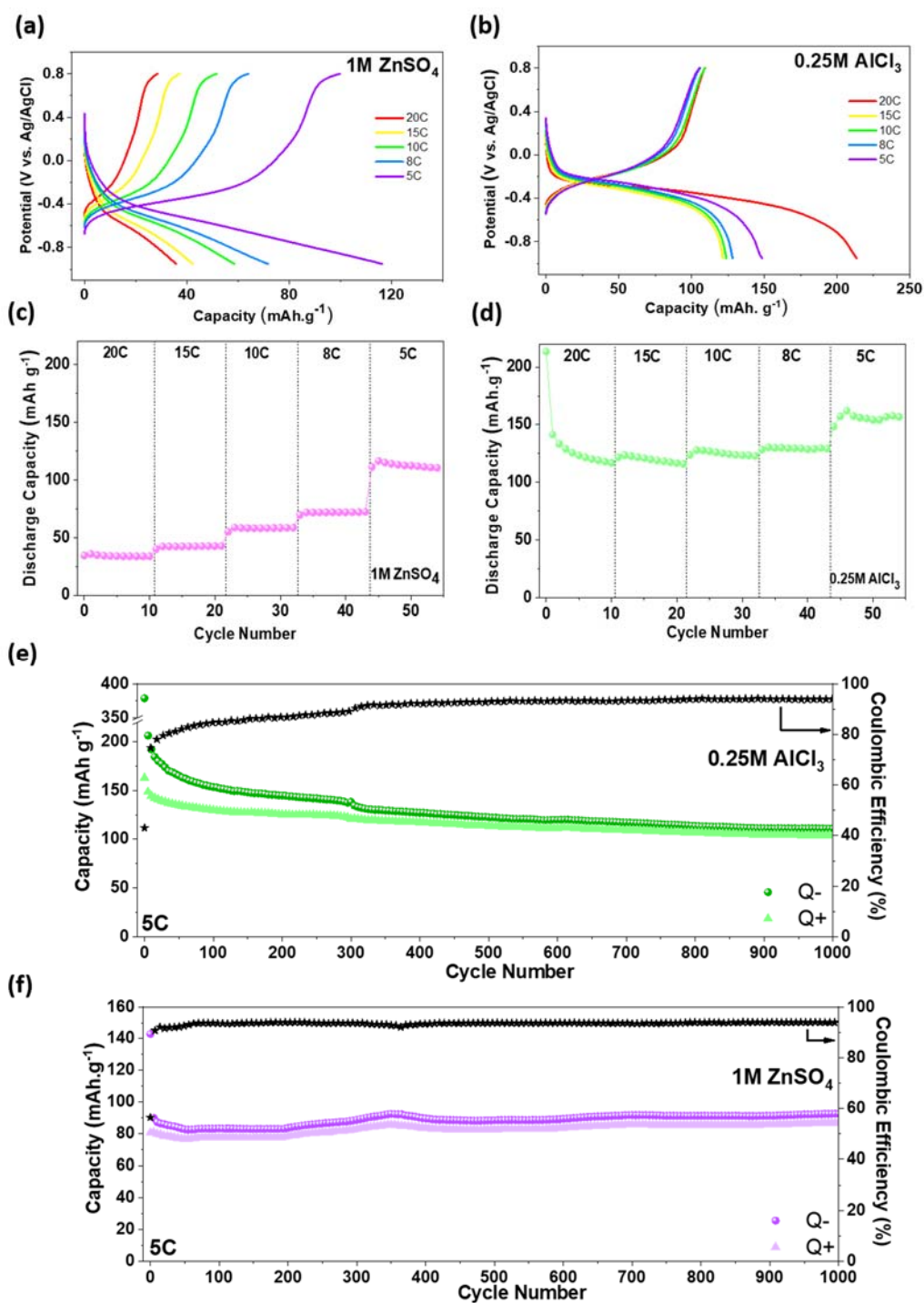


Figure 3: Electrochemical performance of PoPD. Discharge/charge plateau at different current densities in (a) 1 M ZnSO<sub>4</sub> aqueous electrolyte and (b) 0.25 M AlCl<sub>3</sub> aqueous electrolyte. C-rate performances in (c) 1 M ZnSO<sub>4</sub> and (d) 0.25 M AlCl<sub>3</sub>. Long term-cycling performances at a current density of 5C in (e) 0.25 M AlCl<sub>3</sub> and (f) 1 M ZnSO<sub>4</sub>.

The structural stability of the PoPD electrodes after long-term cycling process was shown with the SEM analysis in Figure S3. In comparison with the pristine electrode, there is almost no visible changes observed, revealing their structural integrity. Parasitic reactions in aqueous electrolyte such as the hydrogen evolution and presence of dissolved oxygen,<sup>6, 56</sup> result lower Coulombic efficiencies (CE) and subsequent partial irreversible discharge/charge process in both electrolytes. Moreover, proton uptake/removal rather than zinc has already been reported in ZIBs with organic polymer electrode containing phenazine nitrogen atoms.<sup>57</sup> In aqueous Al<sup>3+</sup> containing electrolytes, a recent study reported the aluminum ions' role in the redox process of PANI electrode, in addition to the proton insertion/(de)insertion and anion (de)doping.<sup>21</sup> In comparison with the other organic electrode materials employed in aqueous electrolyte zinc-ion battery systems, the PoPD conductive polymer as a candidate of organic electrodes exhibited high rate and good cycling performance (Table S1). Notably, organic electrode materials composed of small molecules, macromolecules, or polymeric molecules (through a variety of relatively weak intermolecular interactions such as van der Waals forces, hydrogen bonds,  $\pi$ - $\pi$  interactions, and electrostatic Coulomb forces<sup>11</sup>) are appealing due to their flexibility, environmental friendliness, and the tunable molecular structure. Thus, their zinc ion storage performances have been investigated.<sup>12</sup> However, PoPD electrode was used for the first time in an aluminum-containing aqueous electrolyte in our study. It is noted that compared with the other organic electrodes (Table S2), it provides high capacity at high current density.

Regarding the CE, even though values were later improved, initially lower CE values were obtained (Figure 3) due to the significant imbalance between the potential proton insertion/(de)insertion by PoPD electrode. In order to further understand the role of proton on the CE values, electrochemical performance of PoPD in 0.25 M AlCl<sub>3</sub>+HCl electrolyte (pH=1.54, ionic conductivity=56 mS cm<sup>-1</sup>) was tested. As depicted in Figure S4a, PoPD electrode in 0.25 M AlCl<sub>3</sub>+HCl electrolyte exhibited the first discharge capacity of 632 mAh g<sup>-1</sup> and after 50 cycles discharge capacity decreased to 204 mAh g<sup>-1</sup> with 85% Coulombic efficiency (CE). Thus, dual carrier insertion process improves the electrochemical performance of PoPD

electrode. On the other hand, the CE of PoPD in  $\text{AlCl}_3+\text{HCl}$  electrolyte is even lower than that in pristine  $\text{AlCl}_3$  electrolyte demonstrating the impact of the protons on the CE (Figure S4b) that is in an agreement with a literature report.<sup>58</sup>

Better electrochemical performance of PoPD electrode in 0.25 M  $\text{AlCl}_3$  electrolyte compared to that in 1 M  $\text{ZnSO}_4$  is considered to be related to the hydration-radius and the dehydration energy of the ion participating in the charge compensation process. Considering a charge compensation occurring with dehydrated cations, the ionic radius of  $\text{Al}^{3+}$  (0.5 Å) is relatively smaller than that of  $\text{Zn}^{2+}$  ions (0.74 Å), which is beneficial to acquire a fast ion transfer and advanced rate capability. Taking into account the hydrated radius, hydrated  $\text{Al}^{3+}$  (1.87- 1.90 Å) (aluminum could be the octahedral form of  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  in acidic media)<sup>59-60</sup> is also smaller than that of hydrated  $\text{Zn}^{2+}$  (4.3 Å).<sup>5</sup> As a result of partial dehydration of the octahedral unit of aluminum ( $\text{Al}(\text{H}_2\text{O})_6^{3+} \leftrightarrow \text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+} + \text{H}^+$ ), proton and hydrated aluminum ion with a smaller hydration number are formed, thus proton intercalation into host material could be also plausible.<sup>59</sup> Moreover, the hydration shell of  $\text{Zn}^{2+}$  containing six water molecules, is one of the challenging factor to be accommodated in the host structure,<sup>61</sup> thus slower kinetics in the case of zinc insertion could be expected. EQCM analyses in Section 3.3 have been employed to investigate the nature of the ions dominating the charge storage process.

### 3.3 Investigation of the dissimilarity of performance behavior in $\text{AlCl}_3$ and in $\text{ZnSO}_4$ electrolytes

To analyze the charge storage mechanism of PoPD electrode in both electrolytes, CV analyses at various scan rates of 1, 5 and 10  $\text{mV s}^{-1}$  (Figures S5a and S5c) were conducted. The relationship between  $\log(i)$  vs.  $\log(v)$  (where  $v$  is the potential scan rate) (Figures S5b and S5d) and the detail of the calculation can be found in supporting information Part E. Then, the contribution of the capacitive and diffusion controlled process was estimated according to the following expression:<sup>62</sup>

$$i(V) = k_1 v + k_2 v^{1/2} \quad (\text{Equation 1})$$

where the term of  $k_1 v$  represents capacitive contribution and the other term of  $k_2 v^{1/2}$  corresponds to the effect of diffusion-controlled process. According to Equation 1,  $k_1$  is the slope and  $k_2$  is the intercept of the  $i/v^{1/2}$  vs  $v^{1/2}$  curve (data not shown). As depicted in Figure S6, PoPD demonstrates 59 % and 62 % of capacitive contribution in 1 M ZnSO<sub>4</sub> and 0.25 M AlCl<sub>3</sub> at a sweep rate of 1 mV s<sup>-1</sup>, respectively and the ratio of capacitive contribution gradually increases, as expected, with the rising sweep-rates. The mutual contribution of the surface and bulk processes indicates the pseudocapacitive behavior of PoPD electrodes in both electrolytes.

Although PoPD exhibits similar capacitive and diffusion-controlled behavior in both Zn and Al containing electrolyte, to further evaluate the ion transport mechanism during the electrochemical performance, PoPD electrodes were investigated by EIS in 0.25 M AlCl<sub>3</sub> and 1 M ZnSO<sub>4</sub> aqueous electrolytes, before and after C-rate tests. Figure S7 shows that Nyquist plots of PoPD electrodes in 1 M ZnSO<sub>4</sub> and 0.25 M AlCl<sub>3</sub> exhibit depressed semicircles associated with the charge transfer process, followed by a straight line with a slope of 45° arising due to Warburg impedance in the low frequency region.<sup>63</sup> As was shown in Equations S2 and S3 in supporting information file, ion diffusion coefficient and Warburg coefficient can be calculated from the Warburg impedance.<sup>64</sup> Warburg coefficients were obtained from the linear fit of the plot of  $Z'$  vs.  $\omega^{-0.5}$  for 1 M ZnSO<sub>4</sub> and 0.25 M AlCl<sub>3</sub> aqueous electrolytes illustrated in Figures S8 and S9, respectively. Since the slope of the curve is much lower in Al<sup>3+</sup> containing electrolyte than that of Zn<sup>2+</sup>, both before and after cycling, one could conclude that faster ion diffusion in PoPD electrode takes place in AlCl<sub>3</sub> containing electrolyte than that of ZnSO<sub>4</sub>.

In a next step, EQCM-based analyses were performed to investigate the charge storage mechanism and the dissimilar performance behavior of PoPD in Al<sup>3+</sup> and Zn<sup>2+</sup> containing electrolytes. Figure 4a depicts the CV response along with the microbalance frequency variation of PoPD film in 1 M ZnSO<sub>4</sub> solution. The direction of the sweep has been highlighted with the arrows. Pair of redox peaks situated at -0.5 V and -0.3 V vs. Ag/AgCl can be observed in the CV profile which is well consistent with the Figure 2d and the reported literature.<sup>39</sup> A prominent frequency decrease and increase take place during the reduction



and oxidation, respectively. This signifies either the electro-adsorption/desorption or insertion/deinsertion of the charged species into the PoPD framework, assuming that the microbalance works under the gravimetric regime. The term 'gravimetric regime' is used to describe the conditions where the frequency changes can be converted to the mass changes, according to Sauerbrey equation, which is applicable to thin dense films with flat surface rigidly attached to the quartz resonators' surface (in the absence of solid-liquid hydrodynamic interactions and without any changes in the viscoelastic properties).<sup>29-30</sup> The beginning and end of the frequency variation overlap in Figures 4a and 4c, which indicates the reversibility of the process. The hysteresis in frequency response is assumed to be due to the differences between the kinetic rates of the interfacial species transfer which occurs during the discharge/charge process.<sup>65-66</sup> The stability of the film has been probed with the frequency, charge and current variation with time (Figure 4b), no significant decay was observed except a slight upward trend in the frequency profile. Figure 4a shows the respective data after stabilization of the current. For PoPD film cycled in  $\text{AlCl}_3$  solution, prominent reduction and oxidation peaks can be observed at -0.2 V and -0.15 V vs. Ag/AgCl, respectively (Figure 4c). The frequency variation follows the similar trends like its Zn counterpart, *i.e.*; frequency decrease/increase during a cathodic/anodic scan as shown in Figure 4c. However, unlike Zn, the magnitude of frequency variation observed in this case is much smaller. It is noted that the PoPD films used for tests in  $\text{ZnSO}_4$  and  $\text{AlCl}_3$  have similar loadings (electrodeposited under the same conditions, leading to a thickness of  $\sim 150 \text{ nm}^{40}$ ), therefore the significant difference in  $\Delta f$  response indicates an alteration of the interfacial processes which is interpreted considering different aspects, *i.e.* the nature of the (de)inserted ions, the role of protons and additional surface layer formation. The EQCM response of subsequent cycles has also been shown for the  $\text{AlCl}_3$  electrolyte (Figure 4d) and a reasonable stability over the cycles is observed.

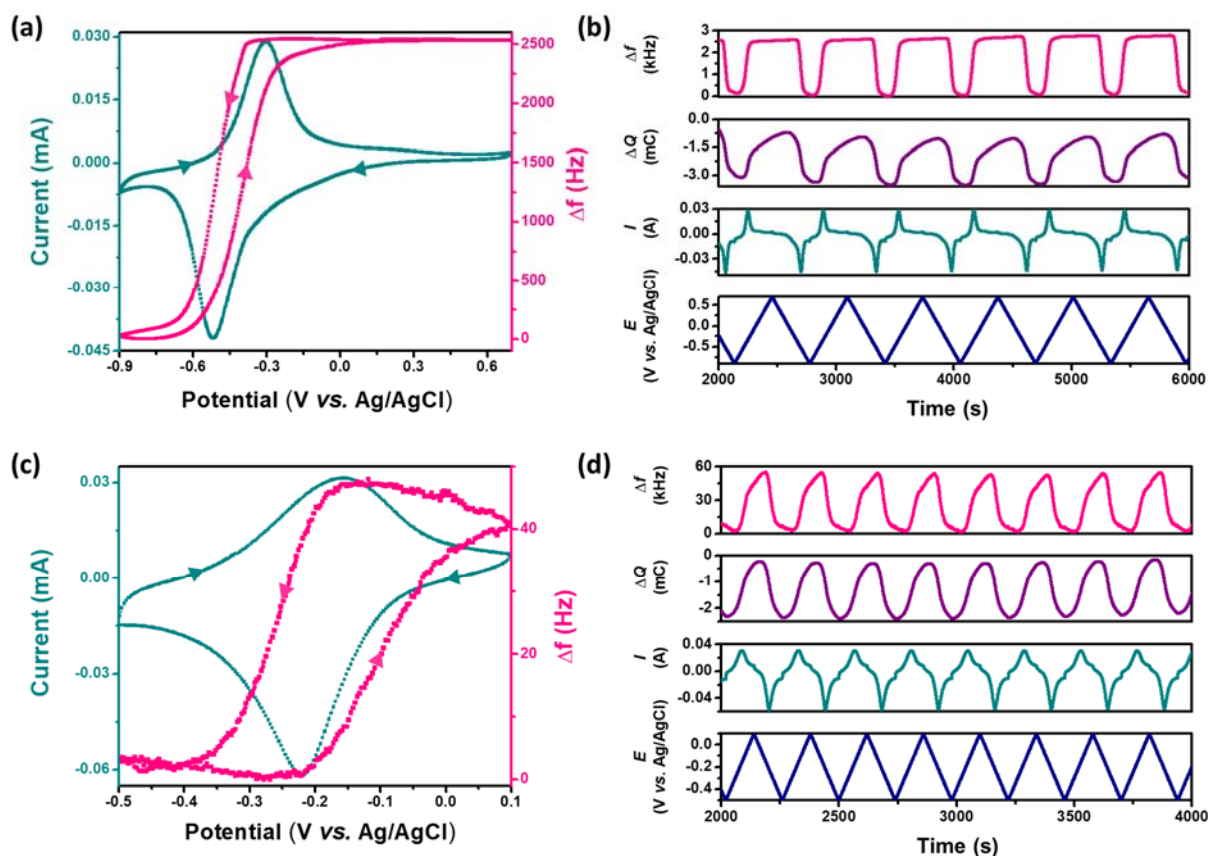


Figure 4: Cyclic voltammogram and microbalance frequency response of PoPD films in (a) 1 M  $\text{ZnSO}_4$  electrolyte and (c) 0.25 M  $\text{AlCl}_3$  carried out at  $5 \text{ mV s}^{-1}$ ; Frequency, charge, current and potential as a function of time for (b) 1 M  $\text{ZnSO}_4$  and (d) 0.25 M  $\text{AlCl}_3$  electrolyte.

Here, we assume that the film is thin enough and strongly attached to the gold electrode of the QCM which enables us to apply Sauerbrey equation<sup>41</sup> under gravimetric regime to convert the  $\Delta f$  into  $\Delta m$  and estimate mass per electron (MPE) values. If the charge transfer process is dominated by only one species, the MPE would be equivalent to its molar mass. To estimate the MPE value,  $\Delta m$  has been plotted as a function of charge variation ( $\Delta Q$ ) and MPE has been calculated from the slope ( $\frac{\Delta m}{\Delta Q}$ ). The corresponding profile of PoPD film cycled in  $\text{ZnSO}_4$  during reduction and oxidation have been depicted in Figure 5a and Figure 5b, respectively. During reduction (Figure 5a), the two different regions (highlighted with shaded area) with lower and higher  $\text{MPE}_{\text{exp}}$  values than that of  $\text{MPE}(\text{Zn}^{2+})$  (*i.e.*,  $32.7 \text{ g mol}^{-1}$ ) have been noticed. During the oxidation, the  $\text{MPE}_{\text{exp}}$  (or the slope ( $\frac{\Delta m}{\Delta Q}$ )) is also significantly higher than that of theoretical

(Figure 5b). On the other hand, in case of  $\text{AlCl}_3$  electrolyte, the MPE values calculated from the mass vs. charge variation are smaller than the MPE of  $\text{Al}^{3+}$  (*i.e.*;  $9 \text{ g mol}^{-1}$ ) during both reduction and oxidation (Figure 5c and 5d). The theoretical MPE values of  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$  have been highlighted with brown straight line in respective plots.

It can be observed that in none of the case, the MPE values are in well agreement with the respective cations, especially for  $\text{Zn}^{2+}$ , the mass variation is vast. To investigate this enormous mass variation, the motional resistance changes ( $\Delta R_m$ ) has also been monitored along with the microbalance frequency and current. Figures S10a and S10b depict the variation of microbalance frequency and motional resistance with time in  $\text{ZnSO}_4$  and  $\text{AlCl}_3$  solution, respectively. The estimated  $\frac{\Delta R_m}{\Delta f}$  gives a maximum value around  $0.05 \text{ } \Omega \text{ Hz}^{-1}$  for  $\text{ZnSO}_4$  and higher than that in  $\text{AlCl}_3$  electrolyte (for the latter the  $\Delta R_m$  is rather small). Figure 5a exhibits a low experimental MPE value during the onset of the reduction process indicates the insertion of  $\text{Zn}^{2+}$  and/or hydrated proton in the PoPD framework, which has been highlighted in green. This highlighted region is shown separately in supporting information (SI) along with the frequency and motional resistance variation (Figures S11a and S11b). At the onset of reduction, the low MPE ( $-12 \text{ g mol}^{-1}$ ) induces small increase in the motional resistance (Figure S11b). Whereas, at the reduction peak, the large MPE suggests species heavier than  $\text{Zn}^{2+}$  is involved, which is supported with the enormous increase in the motional resistance shown in Figure S11b that is an enlarged version from Figure S10a. This substantial  $\Delta f$  and  $\Delta R_m$  can be addressed by the well-known  $\text{Zn}_4(\text{OH})_6\text{SO}_4 \cdot n\text{H}_2\text{O}$  (ZHS) formation during the reduction process at the electrode-electrolyte interface, reported in several literature.<sup>67-71</sup> The ZHS formation can increase the local viscosity at the interface which can perturb the microbalance from functioning as a gravimetric probe. During oxidation, again a MPE value greatly higher than that of  $\text{Zn}^{2+}$  is obtained, and assumed to be a combined contribution from de-insertion of  $\text{Zn}^{2+}/\text{H}_3\text{O}^+$  as well as dissolution of ZHS (Figure 5b). It is emphasized that in Figure 5 the MPE values are only given for the regions where the  $\Delta R_m$  values are small, so that the Sauerbrey equation can be applied. The higher slope

$\left(\frac{\Delta m}{\Delta Q}\right)$  regions (Figure 5a, b, highlighted with pink background) are interpreted considering the ZHS formation/dissolution intervening in the ion intercalation-deintercalation process and the EQCM-R ( $R_m$  monitoring) is used as a qualitative characterization tool for the ZHS formation.<sup>72</sup> The  $\Delta R_m$  values are remarkably reversible (*i.e.*; increase during a cathodic sweep and decrease to initial value on the reverse scan) indicating that the complete dissolution of the ZHS at the end of charge.

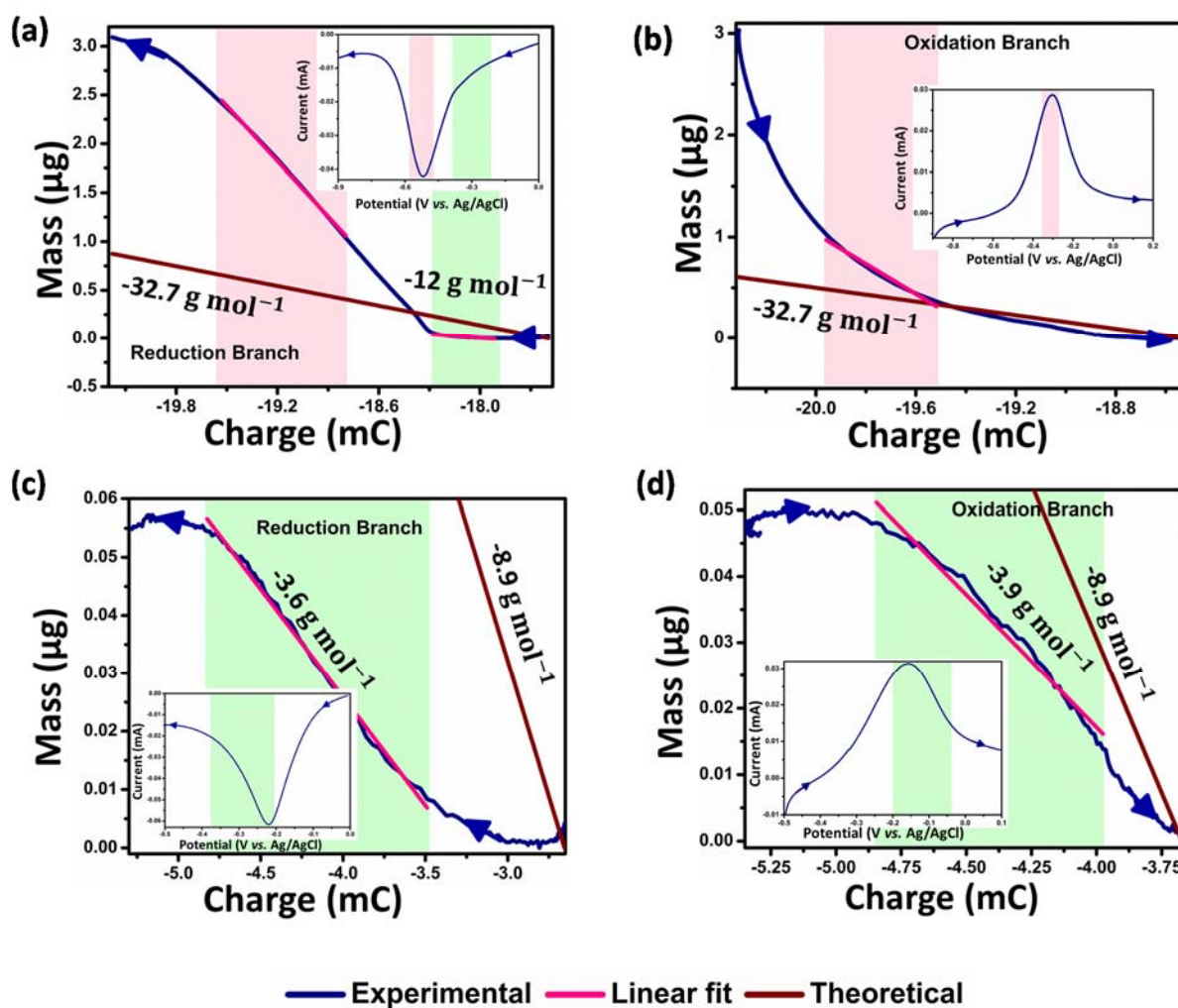


Figure 5: Electrode mass *vs.* charge change during reduction and oxidation, shown for 1 M  $\text{ZnSO}_4$  (a and b) and 0.25 M  $\text{AlCl}_3$  (c and d), respectively. The voltage ranges corresponding to the linear fit in (a to d) have been estimated from the different slopes in the mass *vs.* charge profile.

Along with the EQCM measurements, EDS analyses and *ex-situ* X-ray diffraction tests were performed in order to investigate the ZHS formation of the PoPD electrodes at the end of the 1<sup>st</sup> discharge. EDS spectra depicted in Figures S12a and S12b demonstrate that while there are sharp peaks appeared at the PoPD electrode in Zn containing electrolyte belonging to the Zn, S and O elements, almost no change were observed in AlCl<sub>3</sub>. Although both PoPD electrodes were washed with bi-distillated water, the additional peaks appeared on the surface of the electrode in ZnSO<sub>4</sub> could be assigned to the formation of flake shaped ZHS (Zn<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub>.5H<sub>2</sub>O) structure which is a well-known morphology of zinc sulfate hydroxide<sup>73</sup>. Moreover, EDS mapping of pristine PoPD electrode demonstrates the homogeneous distribution of nitrogen and carbon elements on graphite substrate (Figure S13a). Figure S13b verified the locally covered Zn on the PoPD electrode after fully discharged. The Zn/S mole ratio around 2.5 (calculated from the EDS wt% in Figure S12a) was obtained that is sufficiently close to the ZHS composition. Later, *ex-situ* XRD measurements confirmed the presence of a peak at around 9° corresponding to Zn<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub>.5H<sub>2</sub>O formation after the first discharged state of the PoPD electrode in 1 M ZnSO<sub>4</sub> (Figure 6a, b). Furthermore, in order to elucidate the proton insertion into PoPD, time dependent FTIR analyses (Figure 6c, d) were performed during the first discharge/charge states in 1 M ZnSO<sub>4</sub> electrolyte at a current density of C/2. In the FTIR spectra, it was evident that the most significant intensity variation occurred at 3324 cm<sup>-1</sup> corresponds to N-H bond, the intensity of N-H slightly increased during the discharge, and decreased during the charge state, indicating plausible reversible proton insertion.<sup>57</sup>

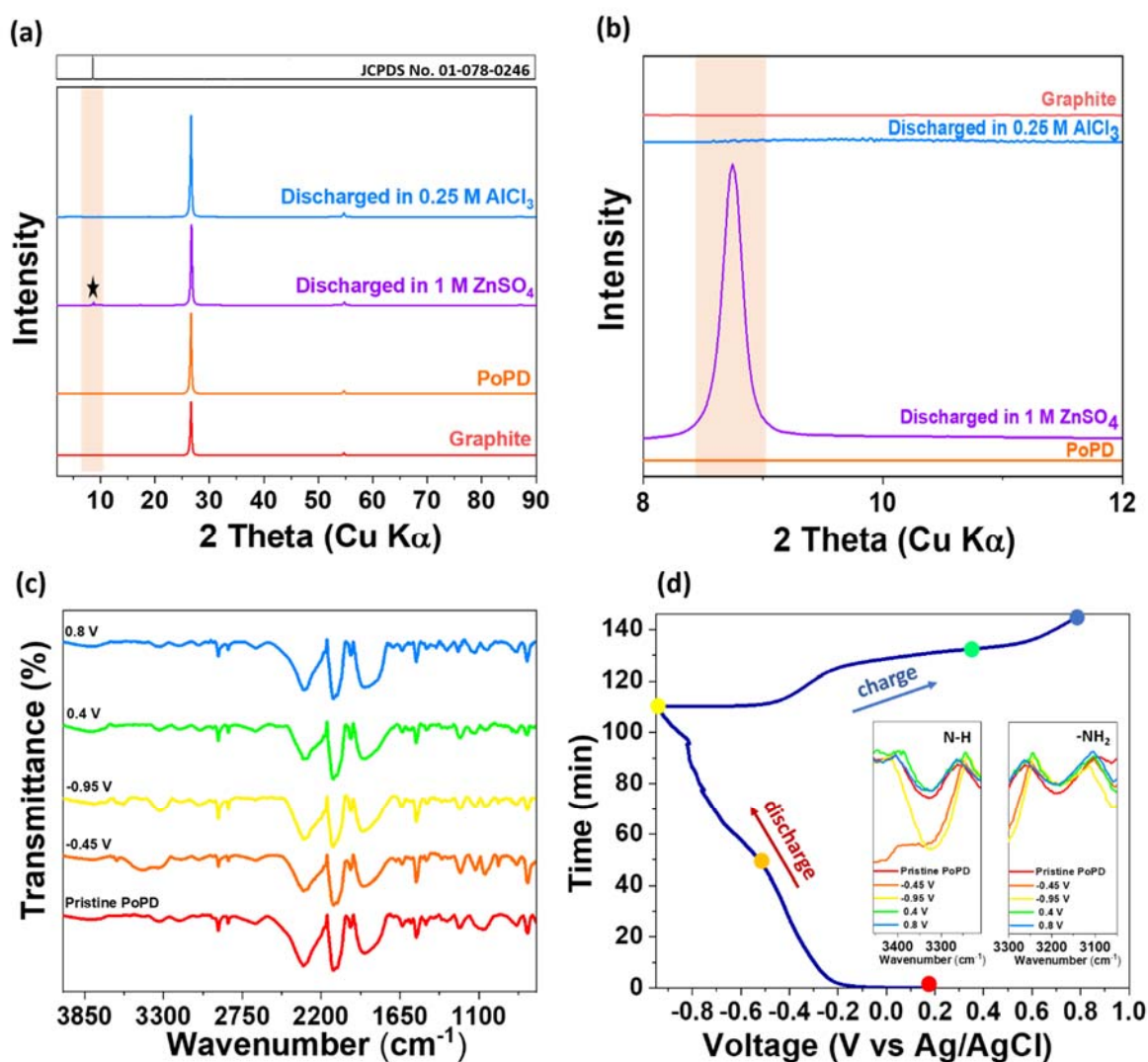


Figure 6: (a) XRD of graphite, PoPD electrode, PoPD at the end of the discharged in 1 M  $ZnSO_4$  and 0.25 M  $AlCl_3$ , (the star symbol demonstrates the characteristic diffraction peak of the formed ZHS) (b) XRD peak analysis zoomed between  $8^\circ$  and  $12^\circ$ . (c) FTIR spectra of PoPD electrode at the pristine and different voltage, (d) time-voltage profile of PoPD in 1 M  $ZnSO_4$  electrolyte and inset images show the peaks of the FTIR spectra between wavenumbers of 3500 and 3000  $cm^{-1}$ .

Unlike the Zn system (Figure S10a), a minor variation of motional resistance in  $AlCl_3$  electrolyte (Figure S10b) indicates that the (de)intercalation of ionic species into the cathode framework does not cause a deviation from the gravimetric regime of the EQCM. Although the calculated MPE values are greater than that of MPE ( $Zn^{2+}$ ) (*i.e.*, 32.7  $g\ mol^{-1}$ ) in the previous system, except on the onset of the reduction peak

(Figure 5a), for AlCl<sub>3</sub> electrolyte, the calculated MPE (-3.6 and -3.9 g mol<sup>-1</sup> for cathodic and anodic scan, respectively) is lower than theoretical MPE of Al<sup>3+</sup> (Figures 5c and 5d). This gives an indication that the Al<sup>3+</sup> species might not be the dominant ionic species and other ions (with different valence and molar mass) may take part in the charge compensation process.

To quantify the partial contribution of the multivalent cations, the charge fraction ( $x = Q_{Al^{3+}}/\Delta Q$ ) has been calculated considering Al<sup>3+</sup> and H<sub>3</sub>O<sup>+</sup> are the ionic species taking part in the redox reaction according to the following equation:<sup>74</sup>

$$\Delta f = \frac{-k_s}{A.F} \left[ \frac{x(\Delta Q * M_{Al^{3+}})}{n_{Al^{3+}}} + \frac{(1-x)(\Delta Q * M_{H_3O^+})}{n_{H_3O^+}} \right] \quad (\text{Equation 2})$$

where  $\Delta f$  is the microbalance frequency variation,  $k_s$  is the experimental sensitivity coefficient (16.3x10<sup>7</sup> Hz g<sup>-1</sup> cm<sup>2</sup>),  $A = 0.2$  cm<sup>2</sup> is the active area of quartz and  $F$  is the Faraday constant,  $\Delta Q$  is the charge variation,  $M_{Al^{3+}}$ ,  $n_{Al^{3+}}$ ,  $M_{H_3O^+}$  and  $n_{H_3O^+}$  represents the molar mass, and the number of transferred electrons by Al<sup>3+</sup> and hydrated protons, respectively. The charge fraction  $x = \frac{Q_{Al^{3+}}}{\Delta Q}$  denotes the fraction of charge compensated by the Al<sup>3+</sup> out of the total charge variation. The calculated charge fraction for Al<sup>3+</sup> ( $x = \frac{Q_{Al^{3+}}}{\Delta Q}$ ) is 0.16 ( $\frac{Q_{H_3O^+}}{\Delta Q}$  is 0.84) and it is well consistent with the MPE analysis. Recent literature also demonstrates that in acidic pH, protons are more likely to participate in the charge compensation than the respective cations present in the electrolyte used.<sup>75-76</sup> A similar estimation can be possible for ZnSO<sub>4</sub> electrolyte but for a more restricted potential range. In Figure S11a, green portion where the absolute value of MPE is 12 g mol<sup>-1</sup>, corresponds to a  $\frac{Q_{Zn^{2+}}}{\Delta Q}$  value of 0.40 over  $\frac{Q_{H_3O^+}}{\Delta Q}$  value of 0.60. This suggests that a more significant contribution of H<sub>3</sub>O<sup>+</sup> in the charge compensation process in AlCl<sub>3</sub> than that happens in ZnSO<sub>4</sub> electrolyte. This dissimilarity in the proportion of the ionic species transferred at the electrode/electrolyte interface may also govern the ionic diffusion in the bulk of the electrode. Although the experiments cannot be directly comparable with the film thickness on graphite electrode, the result

obtained with EQCM is still well consistent with the Warburg coefficient estimations in Figures S8 and S9, where a higher diffusion coefficient was estimated in case of  $\text{AlCl}_3$  electrolyte, as  $\text{H}_3\text{O}^+/\text{Al}^{3+}$  ratio is higher than that of  $\text{H}_3\text{O}^+/\text{Zn}^{2+}$ . For the  $\text{ZnSO}_4$  electrolyte, a relatively smaller portion of  $\text{Zn}^{2+}$  is replaced by  $\text{H}_3\text{O}^+$  and the additional effect of the evolution of the interface with the ZHS formation make the ion diffusion slower than that happens in  $\text{AlCl}_3$ . It has been reported that local change in the pH value resulting from potential proton involvement in the charge compensation process promotes ZHS formation in which at a pH of 5.47 ZHS formation initiates.<sup>77</sup> For the present EQCM-R analysis, the ZHS formation is responsible for the enormous frequency and motional resistance change during cycling. It does not take part in the charge compensation process but our comparative results obtained in  $\text{AlCl}_3$  and  $\text{ZnSO}_4$  electrolytes show that it can affect the ions' interfacial transfer and transport properties. Scheme 1 also demonstrates an illustration of the dissimilar behavior of PoPD in the different electrolytes.

#### 4. Conclusion

Herein, the charge storage performance and interfacial processes occurring at an organic electrode interface, in two different electrolytes containing  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$  multivalent ions were investigated. Among the CP electrodes, a relatively less investigated aromatic diamine-based CP, *i.e.*, PoPD has been studied in detail. The Al/PoPD cell has exhibited better cycling stability with a discharge capacity of 110 mAh  $\text{g}^{-1}$  after 1000 discharge/charge cycles at a current density of 5C than that of Zn/PoPD cell. The plausible reason behind this difference has been probed from different aspects. While the ratio of the capacitive to diffusion-controlled process seems to be unaltered in both electrolytes, the diffusion coefficient estimated from EIS analyses indicated that faster ion diffusion in PoPD electrode takes place in  $\text{AlCl}_3$  containing electrolyte compared to its Zn counterpart. Thus, the challenging task of finding out the nature of these ions was undertaken by EQCM analyses. It revealed a significant contribution of the  $\text{H}_3\text{O}^+$  in the charge compensation process, in addition to the respective multivalent ions. Especially, in the case of  $\text{AlCl}_3$ , it is evident that the contribution of protons dominates over  $\text{Al}^{3+}$ . No anion participation is noticed in both



electrolytes. Proton involvement was further verified by time-dependent FTIR with PoPD electrode cycled in ZnSO<sub>4</sub> electrolyte through the observation of the -NH groups. Later, *ex-situ* XRD measurement revealed the well-known ZHS formation at the end of the discharged state due to the proton insertion accompanied by the local pH increase. Additionally, EQCM explored the formation/dissolution of ZHS at electrode-electrolyte interface during reduction/oxidation, and the motional resistance increase was observed only in ZnSO<sub>4</sub> electrolyte not for AlCl<sub>3</sub> electrolyte. To the best of our knowledge, this work is the first report elucidating the nature of charge carries of an organic electrode, PoPD, in a comprehensive/comparative manner in which both Al<sup>3+</sup>/Zn<sup>2+</sup> ion and H<sub>3</sub>O<sup>+</sup> as co-ions reversibly intercalate/(de) intercalate into/from the PoPD film. Besides the differences of the size of the Al<sup>3+</sup> or Zn<sup>2+</sup> species, the better cycling stability and a higher discharge capacity in aqueous AlCl<sub>3</sub> than that in ZnSO<sub>4</sub> seem to be related to the ZHS formation in the latter electrolyte, which is known to hinder the ion transport, as revealed by EIS analysis of this study. As a whole, PoPD organic electrodes exhibited high-rate capability and excellent cycling stability performance in aqueous electrolyte multivalent systems with a tendency for a better performance in AlCl<sub>3</sub> electrolyte revealing the role of both electrolyte cations as well as non-negligible participation of protons in the charge storage mechanism.

## ASSOCIATED CONTENT

**Supporting Information.** Additional characterization data of PoPD electrodes. Electrochemical tests on the role of proton for the CE values. EDS analyses, XRD measurement and time dependent FTIR spectra of the cycled PoPD electrodes, additional EIS data analyses and EQCM data with motional resistance monitoring.

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### Notes

The authors declare no competing financial interest.

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## TOC graphic for

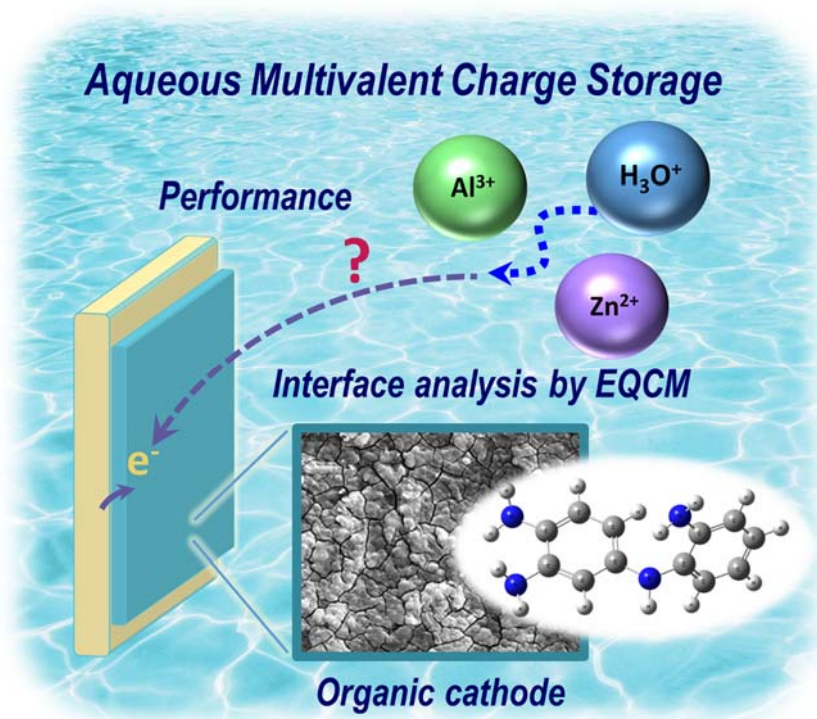
# Aqueous Multivalent Charge Storage Mechanism in Aromatic Diamine Based Organic Electrodes

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# SUPPORTING INFORMATION FOR

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Part A. FTIR spectrum

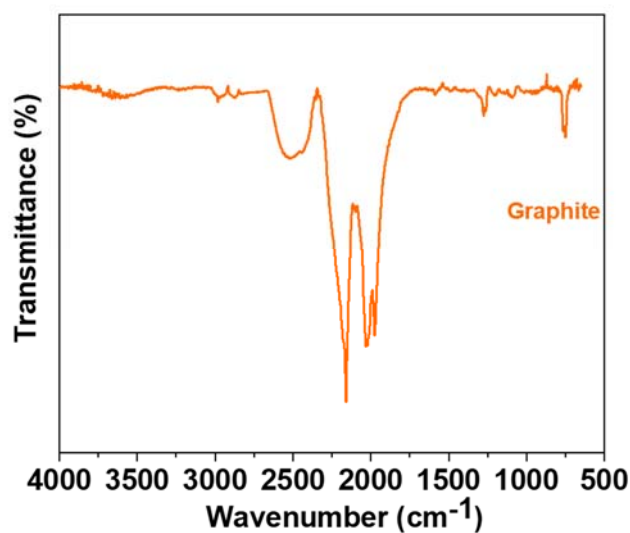


Figure S1. FTIR spectrum of the graphite substrate used in this study.

Part B. Rationalization of the molecular structure of PoPD repeating unit by DFT method

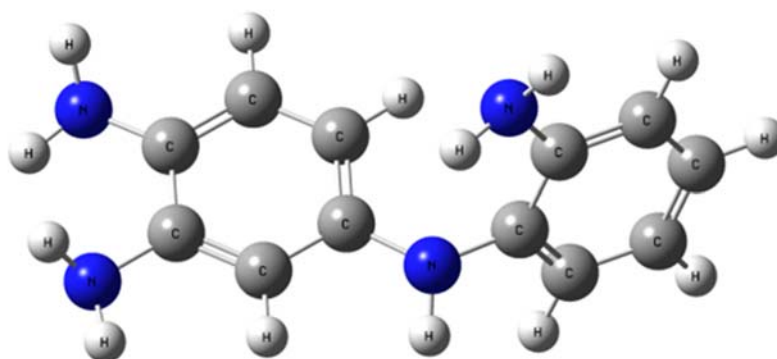


Figure S2. 1,4-substituted benzenoid-quinoid structure of PoPD. Note: blue is N, dark gray is C and light gray is H atoms.

Part C. The structural stability of the PoPD electrodes after long-term cycling process

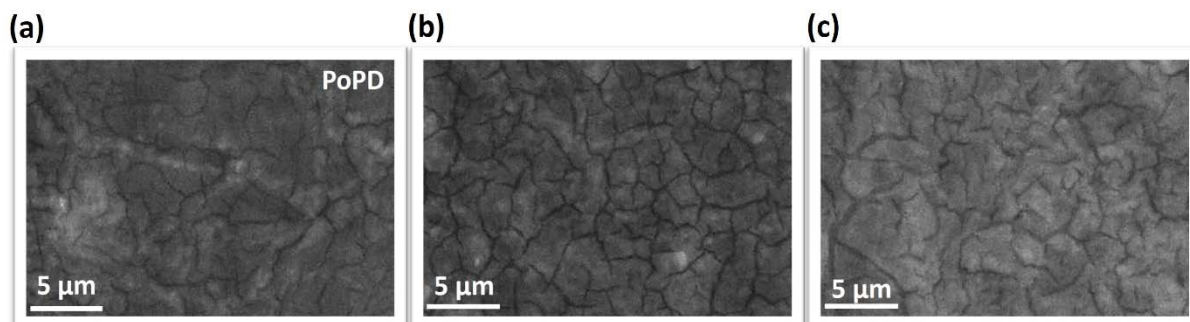


Figure S3. SEM images of (a) PoPD electrode, after long term cycling process (b) in 1 M ZnSO<sub>4</sub> electrolyte, (c) in 0.25 M AlCl<sub>3</sub> electrolyte.

Part D. Experiments on the role of proton for the CE values

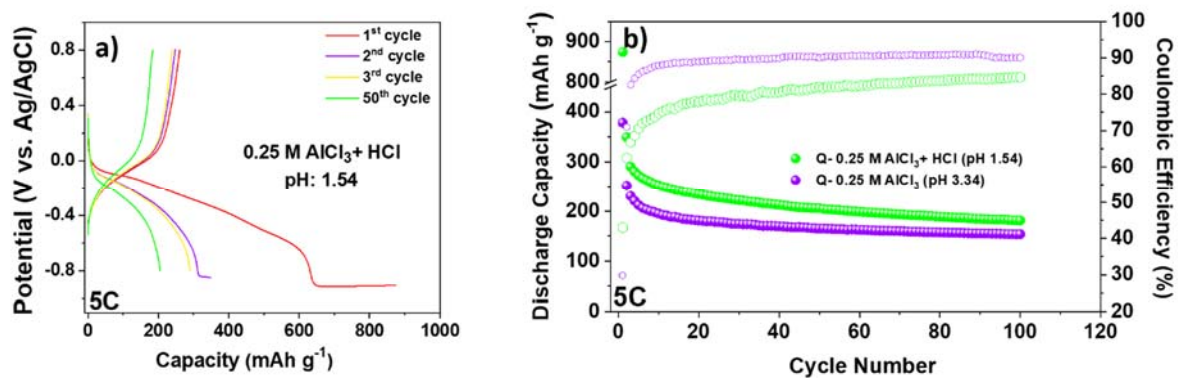


Figure S4. (a) Discharge charge curves of PoPD electrode in 0.25 M AlCl<sub>3</sub> + 0.03 M HCl electrolyte (b) cycling performances at a current density of 5C in both 0.25 M AlCl<sub>3</sub> and in 0.25 M AlCl<sub>3</sub> + 0.03 M HCl electrolytes.

E. The contribution of the capacitive and diffusion-controlled process calculations: the plot of  $\log(i)$  vs.  $\log(v)$  of the PoPD electrodes

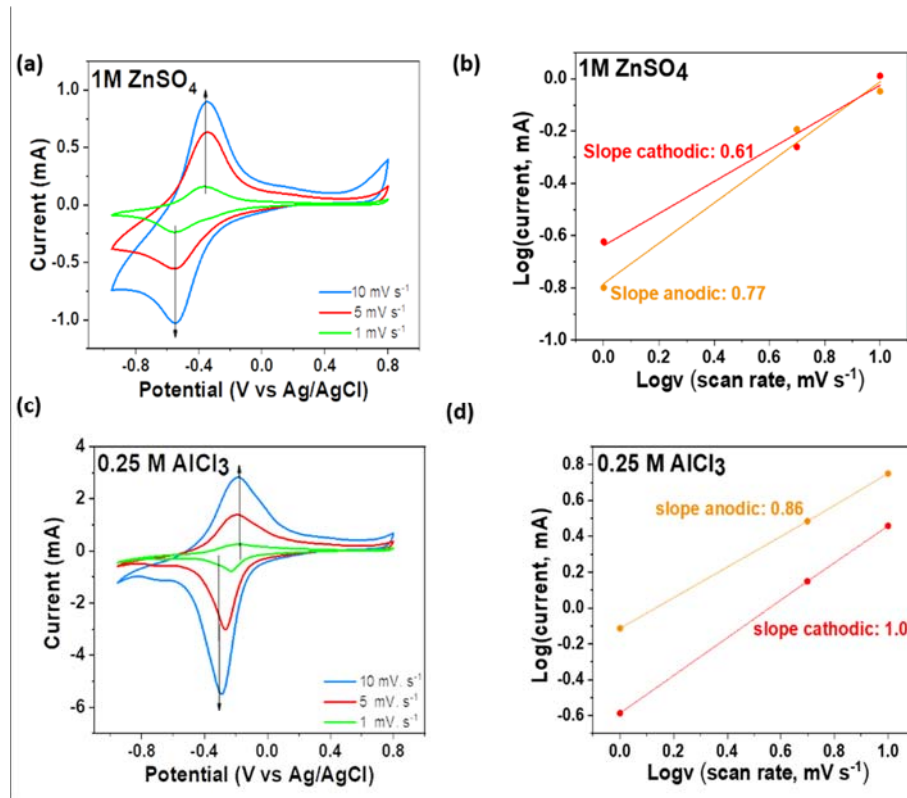


Figure S5: PoPD electrode in 1 M ZnSO<sub>4</sub> electrolyte, (a) CV curves at 1, 5 and 10 mV s<sup>-1</sup> scan rates, (b) the plot of  $\log(i)$  vs.  $\log(v)$ . PoPD electrode in 0.25 M AlCl<sub>3</sub> electrolyte, (c) CV curves at 1, 5 and 10 mV s<sup>-1</sup> scan rates, (d) the plot of  $\log(i)$  vs.  $\log(v)$ .

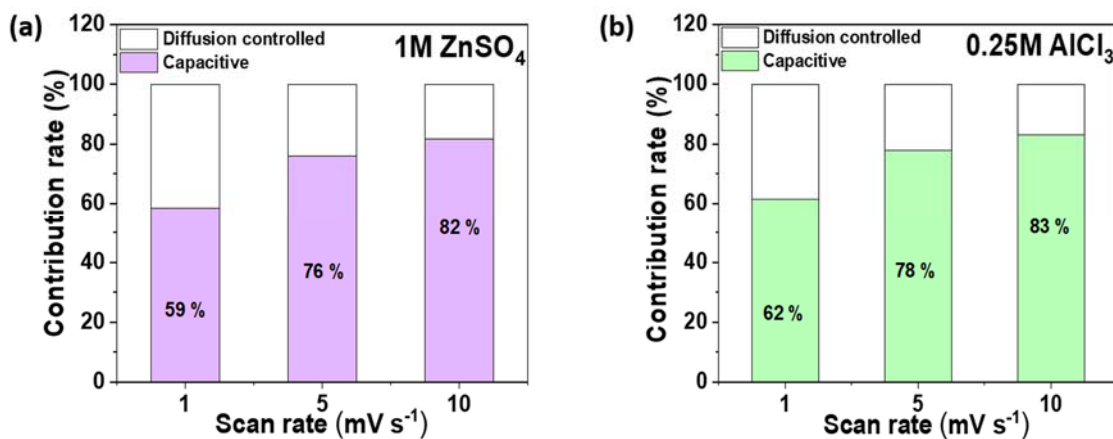


Figure S6: Capacitive and diffusion-controlled contribution at different scan rates of the PoPD electrode on graphite (a) in 1 M ZnSO<sub>4</sub>, (b) in 0.25 M AlCl<sub>3</sub>.

The faradaic, pseudo-capacitance and non-faradaic contribution can be scrutinized by analyzing CV recorded at various scan rates. In Equation S1,  $i$  and  $\nu$  represent the currents values and scan rates, respectively.

$$i = a\nu^b \quad (\text{Equation S1})$$

In this equation,  $a$  and  $b$  are constants in which  $b$  values were determined from the slope of  $\log(i)$  (mA) vs.  $\log(\nu)$  (mV s<sup>-1</sup>) and found 0.61 for anodic and 0.77 for cathodic processes in 1 M ZnSO<sub>4</sub> (Figure S5-b). Likewise, the  $b$ -values of oxidation and reduction from the slope of  $\log(i)$  vs.  $\log(\nu)$  plot (Figure S5-d) in 0.25 M AlCl<sub>3</sub> were calculated as 0.86 and 1.0, respectively. It was described that when  $b$  is near to 1, the capacitive process is dominant in the charge storage mechanism; however, if the  $b$  value is 0.5, diffusion of ionic species (in Al<sup>3+</sup> or Zn<sup>2+</sup> containing electrolytes) mainly control the electrochemical process. Thus, higher  $b$  values for PoPD electrode than 0.5 state that electrochemical reaction is controlled by a capacitive process (surface-controlled). Then, the contribution of the capacitive and diffusion controlled process was estimated and demonstrated in Figure S6.

#### F. Diffusion coefficient estimation by Electrochemical Impedance Spectroscopy

$$D = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2} \quad (\text{Equation S2})$$

where  $R$ ,  $C$ ,  $T$ ,  $A$ ,  $n$ ,  $F$ , and  $\sigma$  represent gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), concentration of ions, absolute temperature (298.15 K), surface area of PoPD (2 cm<sup>2</sup>), electrons transferred, Faraday constant (96500 C mol<sup>-1</sup>), and Warburg coefficient, respectively. Furthermore, Warburg coefficient can be predicted according to the following expression:

$$Z' = R_S + R_{ct} + \sigma \omega^{-1/2} \quad (\text{Equation S3})$$

where  $Z'$ ,  $R_S$ ,  $R_{ct}$  and  $\omega$  indicate value of impedance, resistance between host material and electrolytes, charge transfer resistance and angular frequency, respectively.

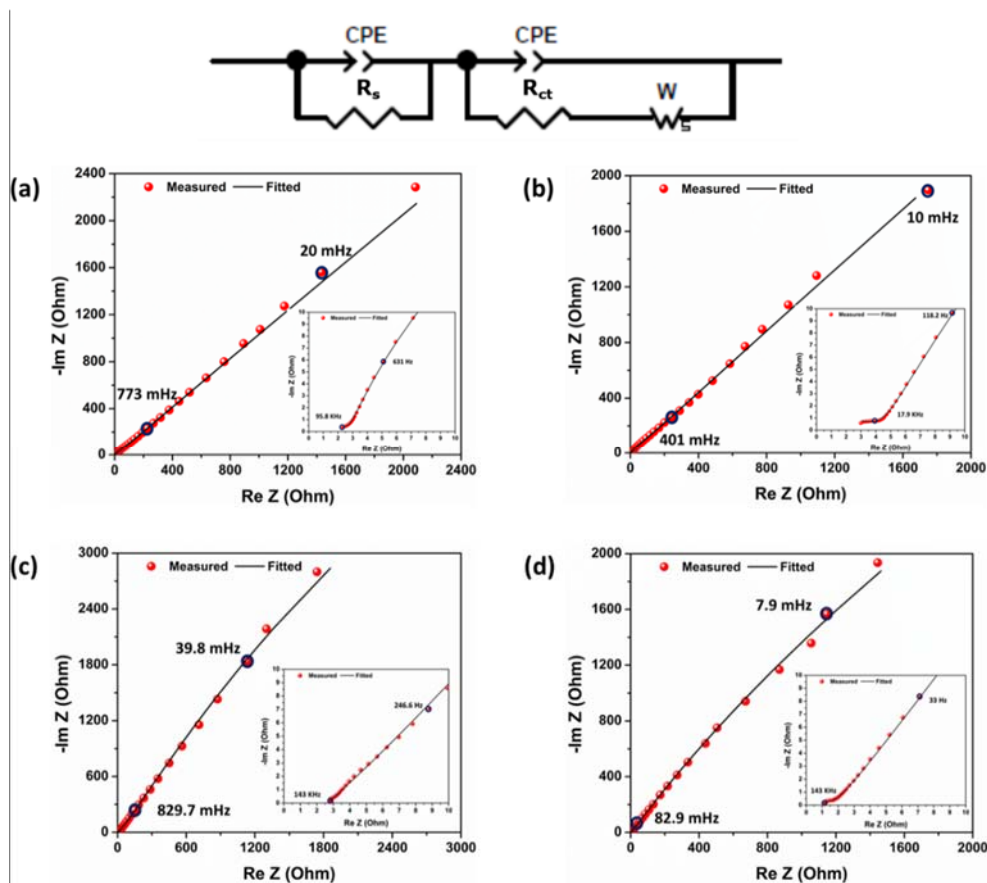


Figure S7: Nyquist plot along with the equivalent circuit (top) of PoPD electrode in 1 M  $\text{ZnSO}_4$  electrolyte measured at initial (a) and final (b) C-rate and in 0.25 M  $\text{AlCl}_3$  electrolyte measured at initial (c) and final (d) C-rate.

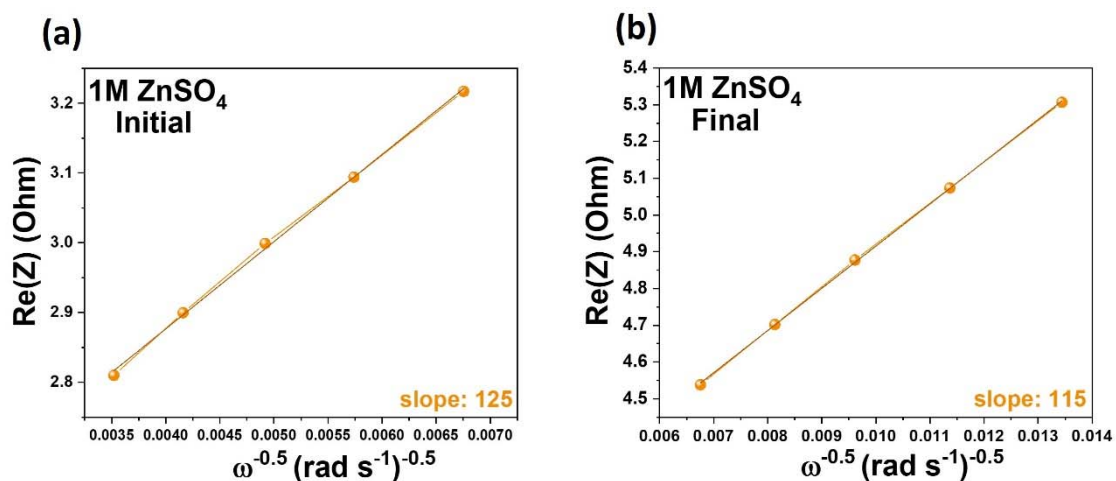


Figure S8: The plot of  $Z'$  vs.  $\omega^{-0.5}$  in the low frequency range of PoPD film electrode in 1 M  $\text{ZnSO}_4$  (a) initial C-rate (b) final C-rate.

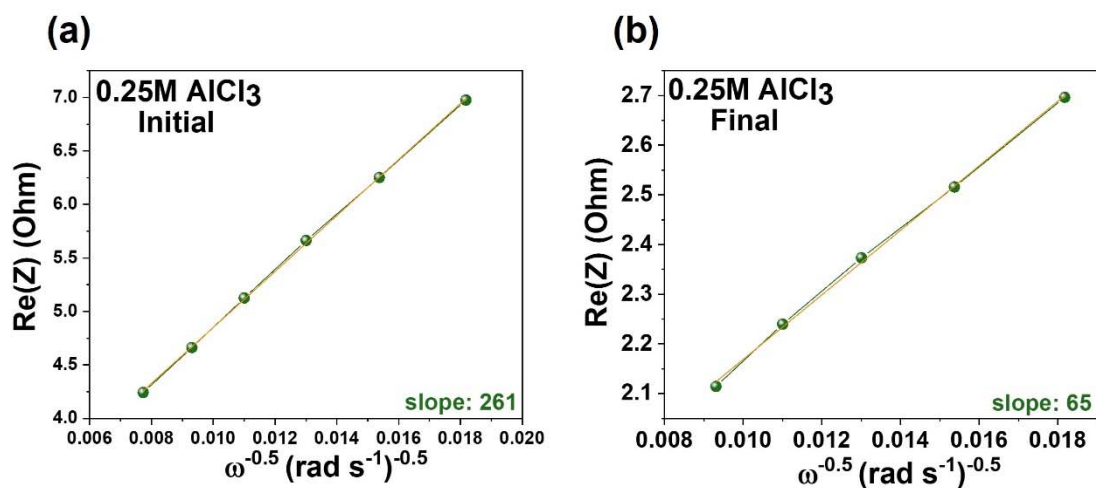


Figure S9: The plot of  $Z'$  vs.  $\omega^{-0.5}$  in the low frequency range of PoPD film electrode in 0.25 M  $\text{AlCl}_3$  (a) initial C-rate (b) final C-rate.

### G. EQCM with motional resistance monitoring of PoPD

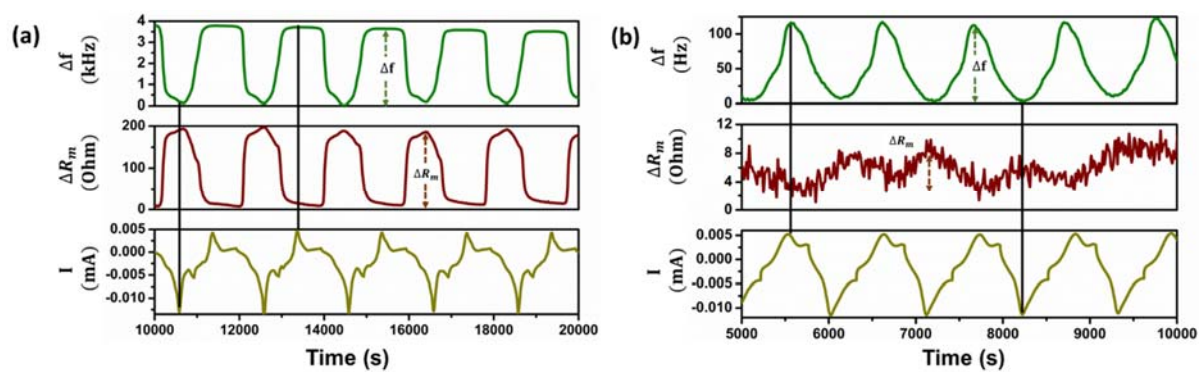


Figure S10: Frequency change ( $\Delta f$ ), motional resistance change ( $\Delta R_m$ ) and current variation with time carried out at a scan rate of  $1\text{ mV s}^{-1}$  in (a)  $1\text{ M ZnSO}_4$  solution and (b)  $0.25\text{ M AlCl}_3$  solution.

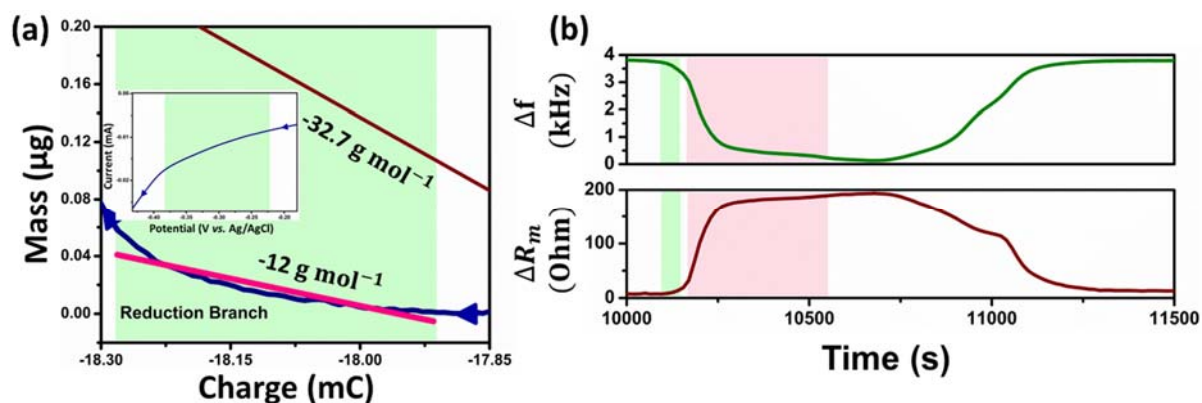
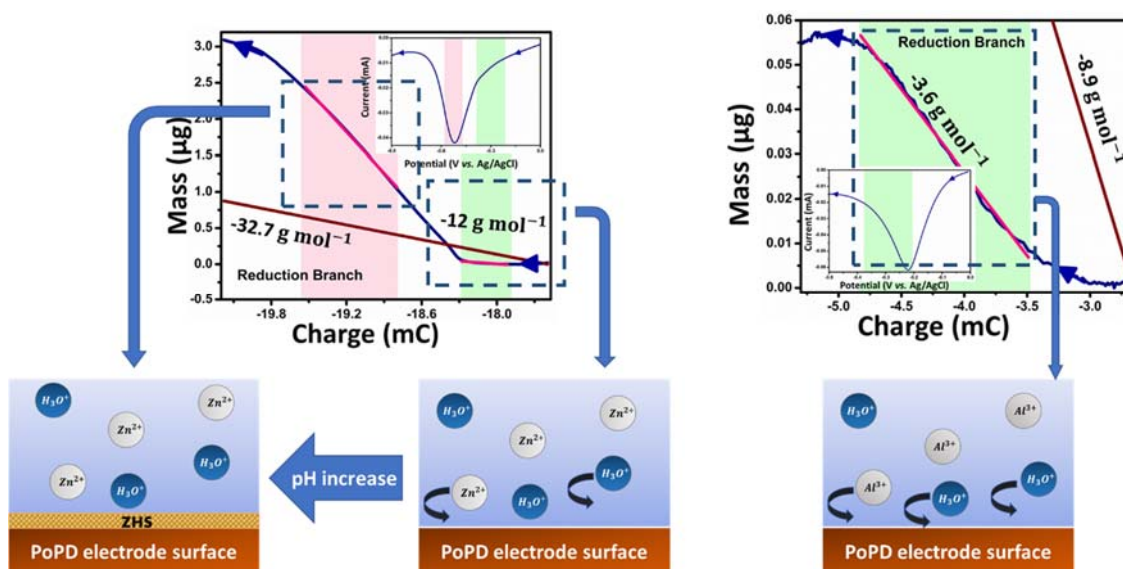


Figure S11: (a) Electrode mass change *vs.* charge during reduction (Enlarged version from Figure 5a in the main manuscript) in (a)  $1\text{ M ZnSO}_4$ ; (b) Frequency change ( $\Delta f$ ) and motional resistance change ( $\Delta R_m$ ) with time (enlarged version from Figure S10a) in  $1\text{ M ZnSO}_4$  solution.



Scheme 1. Schematic description of dissimilar behavior of PoPD in the different electrolytes.



## H. EDX spectrum of the cycled PoPD electrodes

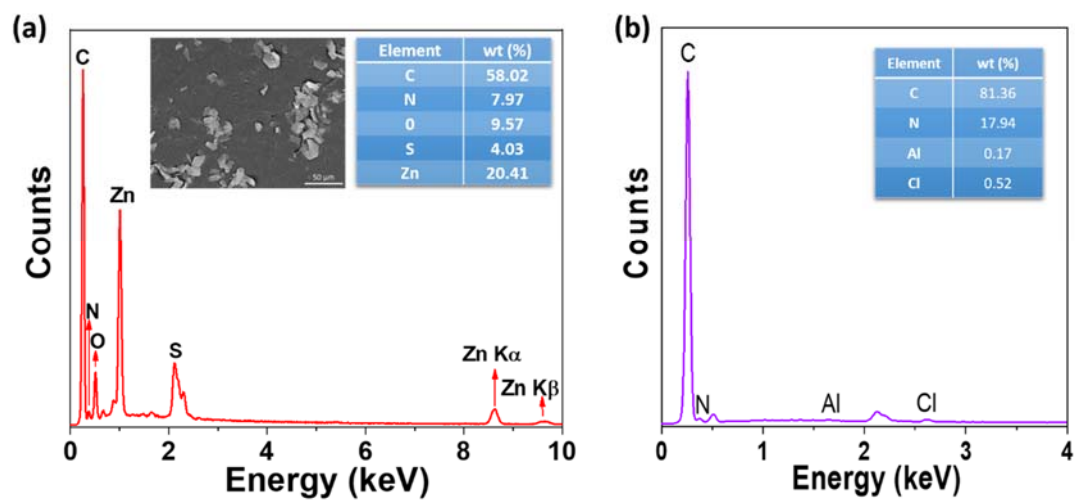


Figure S12: (a) EDS spectrum of PoPD after fully discharged to  $-0.95$  V vs. Ag/AgCl (a) in 1 M ZnSO<sub>4</sub>, (b) in 0.25 M AlCl<sub>3</sub>.

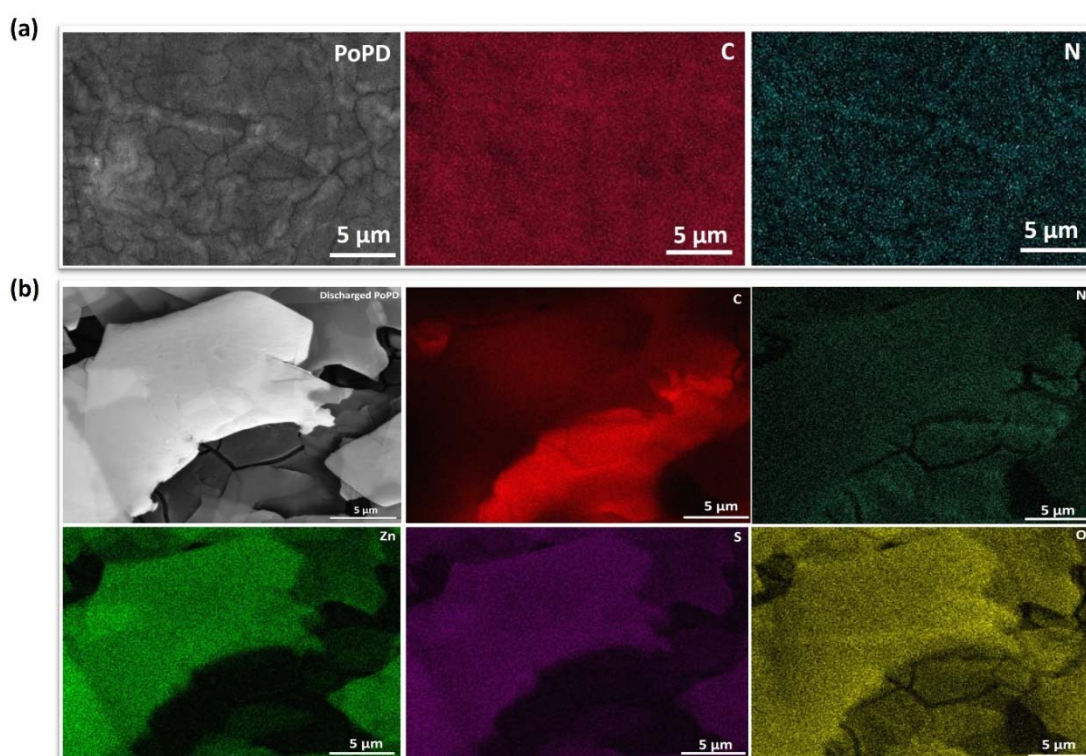
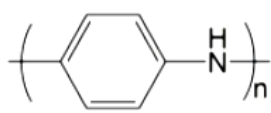
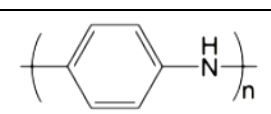
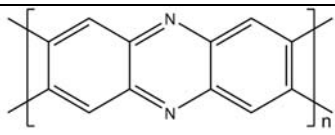
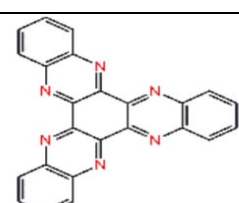
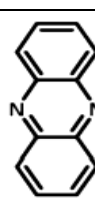


Figure S13. SEM elemental mappings of (a) Pristine PoPD electrode and corresponding elements (C, N), (b) Fully discharged PoPD electrode in 1 M ZnSO<sub>4</sub> and corresponding elements (C, N, Zn, S, O).

## Part I. Literature comparisons

Table 1. Organic cathode materials in aqueous electrolyte Zn-ion batteries

Host Structure	Electrolyte	Discharge capacity, capacity retention, current density, cycle number	Reference
 Sulfo self-doped PANI-S	1 M ZnSO <sub>4</sub>	110 mAh g <sup>-1</sup> , 10 A g <sup>-1</sup> , 2000 cycles	[1]
 PANI/CF	1 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	95 mAh g <sup>-1</sup> , 5 A g <sup>-1</sup> , 3000 cycles	[2]
 PoPD	2 M ZnSO <sub>4</sub>	157 mAh g <sup>-1</sup> , 1 A g <sup>-1</sup> , 3000 cycles	[3]
 diquinoxalino [2,3-a:2',3'-c] phenazine (HATN)	2 M ZnSO <sub>4</sub>	140 mAh g <sup>-1</sup> , 93.3%, 5 A g <sup>-1</sup> , 5000 cycles	[4]
 Phenazine	2 M ZnSO <sub>4</sub>	85 mAh g <sup>-1</sup> , 79%, 1 A g <sup>-1</sup> , 1000 cycles	[5]

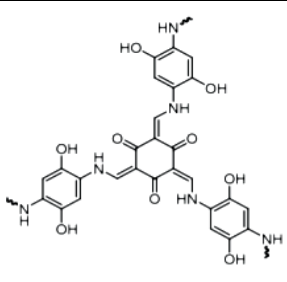


 <p>HqTp</p>	3 M ZnSO <sub>4</sub>	85 mAh g <sup>-1</sup> , 95%, 3.75 A g <sup>-1</sup> , 1000 cycles	[6]
 <p>PoPD (repeating unit)</p>	1 M ZnSO <sub>4</sub>	93 mAh g <sup>-1</sup> , 65 %, 5C, 1000 cycles	This work

Table 2. Organic cathode materials in aqueous electrolyte Al-ion batteries

Host Structure	Electrolyte	Discharge capacity, capacity retention, current density, cycle number	Reference
poly (3,4,9,10-perylenetetracarboxylic diimide) (PPTCDI)	0.5 M AlCl <sub>3</sub>	185 mAh g <sup>-1</sup> , 100%, 100 mA g <sup>-1</sup> , 1000 cycles	[7]
macrocyclic calix[4]quinone (C4Q)	1 M Al(OTF) <sub>3</sub>	333 mAh g <sup>-1</sup> , 81%, 200 mA g <sup>-1</sup> , 50 cycles	[8]
Phenazine	5 M Al(OTF) <sub>3</sub>	132 mAh g <sup>-1</sup> , 76.5 %, 50 mA g <sup>-1</sup> , 300 cycles	[9]
9,10-anthraquinone	1 M Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	211.4 mAh g <sup>-1</sup> , 94.5 %, 800 mA g <sup>-1</sup> , 500 cycles	[10]
tetrachloro-1,4-benzoquinone (TCQ)	1 M Al(OTF) <sub>3</sub>	100 mAh g <sup>-1</sup> , 71.8 %, 2 A g <sup>-1</sup> , 300 cycles	[11]

 <p>PoPD (repeating unit)</p>	0.25 M AlCl <sub>3</sub>	110 mAh g <sup>-1</sup> , 56%, 5C, 1000 cycles	This work
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