Research Article

Electrochemical Mechanism of Al Metal–Organic Battery Based on Phenanthrenequinone

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Received 24 June 2021; Accepted 22 August 2021; Published 1 November 2021

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Al metal-organic batteries are a perspective high-energy battery technology based on abundant materials. However, the practical energy density of Al metal-organic batteries is strongly dependent on its electrochemical mechanism. Energy density is mostly governed by the nature of the aluminium complex ion and utilization of redox activity of the organic group. Although organic cathodes have been used before, detailed study of the electrochemical mechanism is typically not the primary focus. In the present work, electrochemical mechanism of Al metal-phenanthrenequinone battery is investigated with a range of different analytical techniques. Firstly, its capacity retention is optimized through the preparation of insoluble cross-coupled polymer, which exemplifies extremely low capacity fade and long-term cycling stability. *Ex situ* and *operando* ATR-IR confirm that reduction of phenanthrenequinone group proceeds through the two-electron reduction of carbonyl groups, which was previously believed to exchange only one-electron, severely limiting cathode capacity. Nature of aluminium complex ion interacting with organic cathode is determined through multiprong approach using SEM-EDS, XPS, and solid-state NMR, which all point to the dominant contribution of AlCl^{2+} cation. Upon full capacity utilization, Al metal-polyphenanthrenequinone battery utilizing AlCl^{2+} offers an energy density of more than 200 Wh/kg making it a viable solution for stationary electrical energy storage.

1. Introduction

Many developed countries are striving for transfer from fossil-based energy resources towards renewable energy. EU has set an ambitious goal of reducing greenhouse gases emissions by 50% till 2030 and becoming climate neutral in 2050 [1]. However, building renewable energy resources is just the first step, which needs to be accompanied by modification of electric grid. A crucial step is building sufficient stationary energy storage to accommodate all needs from end users which cannot be supported by the renewable energy resources. Hence, energy storage technology plays an important role in this energy transition. Batteries are viewed as an energy storage technology of the future, because they are compact and can be used on dispersed locations alleviating the need for electricity grid upgrade. Among

different battery technologies, Li-ion batteries (LIBs) are currently dominating the market. Contemporary LIBs are based on certain critical raw materials, like Li, Co, Ni, and graphite [2], which raises concerns about their future price, availability, and sustainability. Thus, there is a need for batteries complementary to LIBs, based on abundant and environmentally benign materials.

Multivalent metals like Mg, Ca, and Al are some of the most interesting anode materials due to their high volumetric and gravimetric capacity [3]. Multivalent metals are less prone to dendrite formation, which opens the possibility for the practical application of metal anodes [4, 5]. At the same time, these multivalent metals are among the ten most abundant elements in the Earth's crust, which mitigates sustainability concerns. Unfortunately, intercalation of multivalent metal ions inside inorganic materials is extremely

difficult due to high charge density and consequent strong interaction with inorganic hosts [6]. This can be effectively circumvented by the application of organic materials, which have so far been successfully applied to different multivalent battery systems like Mg, Ca, Al, and Zn [7–12]. Use of organic compounds eliminates the need for use of transition metals that are typically used in Li-ion cathodes. Al metal-organic batteries have recently received a lot of attention due to their ability to circumvent extremely poor electrochemical performance of inorganic cathode materials [10, 12]. Their reversible electrochemical performance was confirmed in a wide range of organic hosts like quinones, conjugated polymers, polyimides, etc. [10, 12–19]. Most of these compounds are n-type compounds, meaning that organic electroactive moieties accept electrons and become negatively charged during discharge leading to interaction with positively charged aluminium species. The exact nature of these species can be different, although the current findings show that complete dissociation of chloroaluminium species to Al^{3+} is not obtained in AlCl_3 -based electrolytes [10, 20, 21]. However, the nature of the electroactive Al species that are interacting with the negatively charged organic moieties has a crucial effect on the anode capacity through the amount of AlCl_3 -based electrolyte needed to form electroactive aluminium species. High utilization of AlCl_3 severely reduces the anode capacity (detailed calculations in the SI). In fact, the anode capacity becomes mainly governed by the amount of AlCl_3 consumed for the formation of chloride containing Al species. In the most common Al electrolyte based on the ionic melt of AlCl_3 and ethyl-methylimidazolium chloride (EMIMCl) with the highest attainable concentration of AlCl_3 , the anode capacity for active ion AlCl_4^- is only 48.6 mAh/g [22]. The anode capacity increases to 94.2 mAh/g for AlCl_2^+ and reaches a maximum value for monochloroaluminium species AlCl^{2+} of 344 mAh/g. Although there is a sevenfold difference between the anode capacity for AlCl_4^- and AlCl^{2+} , the higher value is still an order of magnitude smaller than the capacity of the metal anode in a cell utilizing Al^{3+} cations (2980 mAh/g). This states a clear need to utilize monochloroaluminium or move beyond chloroaluminium species if high energy density Al rechargeable batteries are targeted. Currently, most of the studies employing organic cathodes report utilization of AlCl_2^+ [10, 16, 19], while for cathodes based on anthraquinone (AQ) our group reported AlCl^{2+} [12, 20]. One group even claimed utilization of Al^{3+} in AQ, although the data presented pointed toward the employment of chloroaluminium species [18]. Another interesting phenomena was reported by Choi et al. [10, 13, 21], who claimed only one-electron reduction of phenanthrenequinone group (PQ). This finding is in stark contrast with results obtained in Li metal-organic cell, where 2-electron reduction of PQ electroactive group is regularly observed [23, 24].

In the present work, we investigate the electrochemical activity of PQ in Al batteries, both for PQ monomer and PQ-based polymer polyphenanthrenequinone (pPQ). Furthermore, we synthesized different discharged analogues of PQ active compounds to relate them to different electroactive species inside organic cathode during electrochemical

characterization. The electrochemical mechanism is investigated using a multitude of complementary spectroscopic techniques: IR spectroscopy, X-ray photoelectrons spectroscopy (XPS), ^{27}Al solid-state magic-angle spinning (MAS) NMR, and energy dispersive X-ray spectroscopy (EDS).

2. Experimental

2.1. Synthesis. PQ monomer was purchased from a commercial source (ABCR, 95%). PQ-based polymer was synthesized according to the indirect cross-coupling polymerization reaction [25]. Briefly, PQ was brominated, reduced, protected, and afterwards polymerized through cross-coupling reaction. After polymerization, the intermediate was deprotected and finally oxidized to obtain a final polymer. To improve the electrochemical utilization, we added reduced graphene oxide into the polymerization reaction mixture. Discharge analogues of PQ monomers were obtained through reduction of PQ with $\text{Na}_2\text{S}_2\text{O}_4$. Obtained product phenanthrene-9,10-diol was dissolved in THF and then reacted with different commercial chloroorganoaluminium compounds in hexanes with different ratios between Al and Cl (EtAlCl_2 , Me_2AlCl , AlMe_3). Subsequently, the reaction mixture was dried to obtain different phenanthrene-9,10-dioxy salts (PQ-2AlCl_2 , PQ-AlCl , $\text{PQ}_3\text{-Al}_2$).

2.2. Electrochemical Characterization. Al electrolyte was prepared by gradual addition of AlCl_3 (Aldrich 99.99%) to EMIMCl (Acros 97%) with continuous stirring. Afterwards, Al foil was added to the electrolyte and mixed overnight. A supplementary Al electrolyte based on the mixture of AlCl_3 :urea = 1.3 was prepared according to the reported procedure [26], electrochemical results obtained using this electrolyte are represented in Figure S7. Electrodes were prepared by mixing the active material, Printex XE2 carbon black, and polytetrafluoroethylene (PTFE) binder in ratio 6:3:1. All the components were mixed in Retsch PM100 planetary ball mill for 30 min at 300 rpm in isopropanol. Afterward, the electrode composite was rolled into self-standing electrodes with a diameter of 12 mm, which were later pressed onto molybdenum current collectors. Unless noted, the average active material loading was around 1 mg/cm². Polyvinylidene fluoride- (PVDF-) based electrodes were prepared by mixing the active material, Printex XE2, and PVDF binder in NMP with a planetary ball mill at 300 rpm for 30 min. Afterward, the electrode ink was drop casted on Mo current collectors and dried at 80°C in vacuum. Electrochemical characterization was performed in pouch type cells with molybdenum current collectors (Alfa Aesar 99.95%) and glassy fiber separators (GF/A Whatman) wetted with 60 μl of electrolyte. All electrochemical cells were cycled in the voltage window from 0.8 to 1.8 V at different C-rates, with 1C being defined as 260 mA per g of active material.

2.3. Material Characterization. Prepared compounds and *ex situ* electrodes were characterized using Bruker Alpha II spectrometer equipped with Ge ATR window inside an Ar-filled glove-box. The ATR-IR spectra were collected in absorbance mode with 48 scans at a resolution of 4 cm⁻¹ in

the range of 4000–650 cm^{-1} . *Operando* ATR-IR spectroscopy was performed on Bruker Vertex 80 equipped with a Specac Silver Gate Ge ATR crystal and with liquid nitrogen cooled mercury cadmium telluride (MCT) detector, using a specifically designed pouch cell with Si wafer window [27, 28]. Spectra in *operando* mode were collected with a series of consecutive scans, every 1 min during galvanostatic cycling at 0.5C rate. Scanning electron microscopy (SEM) was performed on FE SEM Supra 35 VP Carl Zeiss. EDS was performed at 20 kV. X-ray diffraction (XRD) was measured on Si sample holder using PANalytical X'Pert PRO MPD with Cu $\text{K}\alpha_1$ in the range from 5 to 65°. PHI Versa-ProbeIII system was used for X-ray photoelectron spectroscopy (XPS). The X-ray source was monochromatic Al $\text{K}\alpha$ (1486.7 eV), and the concentric hemispherical analyzer was positioned at 45° angle from the sample normal. Solid-state NMR experiments were performed with a 600 MHz Varian VNMRs spectrometer, using a 3.2 mm CPMAS probe. Larmor frequency for the investigated ^{27}Al nuclei was 156.18 MHz, and aqueous AlCl_3 solution was used as an external reference. The samples were loaded into a zirconium oxide rotor inside the dry box under a controlled argon atmosphere and spun with magic-angle spinning (MAS) frequencies of 20 kHz for the monomer PQ analogues and 16 kHz for the electrode samples. ^{27}Al MAS NMR spectra were acquired at 25°C, recording 100 000 scans with a pulse length of 0.6 μs and recycle delay of 50 ms. ^{27}Al triple-quantum MAS (3QMAS) NMR spectra were collected applying a three-pulse sequence with z-filter, consisting of a 5.2 μs excitation pulse, a 1.35 μs conversion pulse, and a 20 μs selective 90° pulse, employing rotor synchronization. A total number of 60 points in the indirect dimension with increments of 10.4 ms were obtained; each point corresponds to 10 000 scans. Spectra acquisition was performed with the recycle delay of 50 ms. Data processing was carried out by applying a shear transformation in the indirect dimension. All the electrodes used for *ex situ* characterization were cycled for at least 60 cycles to achieve good capacity utilization of active material. Afterwards, cells were disassembled inside the glove-box and washed two times with THF.

3. Results and Discussion

As a starting point of our work, electrochemical cycling of PQ monomer was performed. In literature, cycling of PQ exhibited relatively low capacity utilization, well below 50% of the theoretical capacity (257 mAh/g) [10, 13], leading to the conclusion that PQ electroactive moiety can undergo only single-electron reduction. This was in stark contrast with our electrochemical cycling results of a similar AQ compound, which is an isomer of PQ. AQ displayed capacity utilization over 70%, clearly indicating two electron reduction of AQ. A clear difference between our and literature work was use of different binders [12, 13]. In our work, PTFE binder was used, while literature results were obtained on electrodes with PVDF binder. To test the possible influence of the binder, PQ electrodes with PTFE binder were prepared. In the first discharge, our PQ electrode gave a high discharge capacity of 176 mAh/g with an average discharge

voltage of 1.35 V (Figure 1). Practical capacity utilization of 68% clearly points to two-electron reduction of PQ electroactive group. In the case of single-electron reduction a maximum of half of theoretical capacity could be expected. However, in practice, first discharge capacities of simple organic compounds are typically much lower than theoretical due to rapid dissolution of active material. The discharge capacity displayed a small drop to 169 mAh/g in the second cycle, which was followed by an accelerated capacity fade due to the dissolution of active material, resulting in only 36 mAh/g of discharge capacity in the 20th cycle. During the remainder of the cycling, Coulombic efficiency stabilized around 98% (Figure 1). To further check for the possible presence of side reactions, electrode composed of only Printex carbon black and PTFE was cycled, exhibiting only capacitance behavior (Figure S1). The redox potential of PQ exemplifies an expected upshift in comparison with AQ electroactive moiety due to the ortho position of carbonyl groups [29]. Interestingly, the overpotential of Al-PQ is relatively high (more than 200 mV), much larger than in the case of AQ (less than 100 mV) [12].

From the obtained discharge capacities, we can assume that PQ undergoes two-electron reduction, which appears as a single voltage plateau. The contrast between our results and those in the literature is most likely caused by use of different binders. To test this hypothesis, we prepared PVDF-based electrode. Electrochemical cycling of PVDF-electrode showed significantly worse electrochemical performance. In the first discharge, only 136 mAh/g is obtained. The capacity fade is even faster than in the case of PTFE-electrode, and less than 50 mA/g is obtained after 5 cycles (Figure S2). The electrode with PVDF binder exhibits also increased polarization of more than 300 mV. An important difference between PVDF and PTFE binders is that PVDF binder is solubilized during electrode preparation, while PTFE is used as a suspension. During ball milling, PTFE binder forms fiber like structures that lead to the highly porous electrode structure. On other hand, soluble PVDF binder glues the particles together giving a less porous electrode structure (Figure S3). From this we can clearly conclude that the use of PTFE binder is beneficial for capacity utilization of the active material, although it does not lead to any long-term stability improvement. Subsequently, PTFE electrodes were used in all further tests.

ATR-IR mechanism investigation was attempted on the *ex situ* PQ electrodes (Figure S4). *Ex situ* characterization is quite challenging due to the solubility of PQ monomer, which prevents the removal of excess electrolyte with solvent washing. In the discharged state, the pristine carbonyl peak at 1674 cm^{-1} completely disappears, and there is a new double peak appearing at 1350 and 1337 cm^{-1} that could be assigned to C-O^- stretching. However, due to the presence of the electrolyte, it is difficult to differentiate between the peaks belonging to PQ or electrolyte. Discharge peaks lose their intensity in the oxidation, and we end up with a spectrum that is similar to the spectra of the electrode soaked into Al electrolyte displaying a very broad peak around 1560 cm^{-1} , which

FIGURE 1: Electrochemical cycling of PQ monomer at 0.5C current density. (a) Selected galvanostatic cycles and (b) capacity and Coulombic efficiency of the Al-PQ cell.

contains contributions of both electrolyte and electroactive PQ group. Overall, the presence of Al electrolyte prevents us from acquiring any definitive conclusions. The spectrum of the discharged electrode also does not fit directly with any of the synthesized discharged analogues of PQ, which were prepared by chemical reduction of PQ to H_2PQ and their subsequent chemical reaction with organochloroaluminium compounds to give PQ-2AlCl_2 , PQ-AlCl , and $\text{PQ}_3\text{-Al}_2$. All of the discharged analogues of PQ display a pronounced C-O^- peak at 1372 cm^{-1} (Figure S5). The position of -C-O^- band is not affected by the type of aluminium counter ion, while a majority of the peaks are slightly shifted between different discharged analogues.

Insoluble active material would stabilize the capacity retention and simplify the *ex situ* characterization of the electrodes by enabling electrode washing. Polymerization of electroactive groups is the most effective approach, which decreases solubility through an increase of molecular weight of the molecules. Indirect cross-coupling polymerization of PQ groups was chosen, since it allows us to synthesize polymer without decreasing the theoretical capacity caused by the introduction of electrochemically inactive linkers. While AQ, having lower redox potential, can be directly cross-coupled with $\text{Ni}(\text{cod})_2$ cross-coupling agent, the higher redox potential of PQ leads to oxidation of cross-coupling agent. Hence, multistep indirect polymerization was utilized [25]. To optimize the electrochemical wiring of the polymer, we added a reduced graphene oxide during the polymerization reaction. Polyphenanthrenequinone (pPQ) polymer was characterized using ATR-IR, XRD, and SEM (Figure S6-8).

During initial cycling, pPQ displays gradual capacity activation; the initial discharge capacity is only 24 mAh/g, but it quickly increases to 116 mAh/g in the first twenty cycles (Figures 2(a) and 2(b)). The subsequent increase of the capacity is more gradual, and a maximum capacity of 168 mAh/g is obtained in the 180th cycle. Coulombic efficiency in initial cycles was above 100% due to capacity acti-

vation of pPQ and the fact that pristine active material is synthesized in the charged state. Afterwards, Coulombic efficiency stabilized and remained above 99% throughout the cycling. After stabilization of the capacity, fading is extremely low with an average drop of 0.025 mAh/g per cycle. This is a considerable improvement over the capacity retention of poly (anthraquinonyl sulfide) polymer (PAQS), which displayed an average drop of 0.14 mAh/g per cycle [12]. The gradual capacity activation of the pPQ polymer was observed before in Mg electrolytes [24] and can be most likely attributed to more complex solvation structure of multivalent electrolytes and, hence, worse ionic accessibility. Electrochemical performance of electrode with high active material loading (6 mg/cm^2) was tested, giving a maximum discharge capacity of 130 mAh/g (Figure S9), opening the door for further optimization of areal capacity.

As a next step, we decided to investigate the rate capability of pPQ polymer (Figures 2(c) and 2(d)). To reduce the effect of gradual capacity activation, we performed 30 cycles at a lower cycling rate of 0.5C. The capacity retention at intermediate rates of 1C and 2C was good but decreased considerably at 5C. At 10C, the capacity dropped to 30 mAh/g, and at 20C, only 8 mAh/g was retained, after return to 0.5C electrode capacity completely recovered. To complement the testing in EMIMCl-based electrolyte, an alternative Al electrolyte based on low-cost chemical such as urea was used [26]. Testing in $\text{AlCl}_3\text{:urea} = 1.3$, electrolyte (Figure S10) displayed a similar electrochemical performance with a maximum capacity of 158 mAh/g. In contrast, Coulombic efficiency was around 99% in the first 100 cycles and then started to drop reaching only 90% after 400 cycles. This points to lower oxidative stability of urea-based electrolyte, which can be also observed as side reactions above 1.7 V in later cycles. Rate capability test gave similar capacity retention as EMIMCl-based electrolyte.

The insolubility of pPQ polymer allowed us to characterize *ex situ* electrodes without the interference of electrolyte

FIGURE 2: (a) Discharge capacity and Coulombic efficiency of pPQ cathode during long-term cycling at 0.5C and (b) selected galvanostatic cycles. (c) Discharge capacity and Coulombic efficiency of pPQ cathode during rate capability test (0.5C-20C) and (d) selected galvanostatic cycles at specific rates (last cycle at specific rate is displayed).

contributions. Among the different solvents (tetrahydrofuran (THF), dichloromethane, and toluene) tested for electrolyte removal, THF has the highest removal capability, although it was still not able to remove 100% electrolyte in washing tests (Table S1). In the discharged electrode, the signal/noise ratio is low (Figure S11); however, it still enables observation of the almost complete disappearance of carbonyl peak at 1678 cm^{-1} and formation of two very broad peaks centered at around 1540 and 1480 cm^{-1} , with poorly resolved contributions between 1400 and 1350 cm^{-1} . In the charged cathode, the intensity of new peaks decreased, and a carbonyl peak at 1678 cm^{-1} reemerged, which points to good reversibility of the carbonyl group. The most prominent peaks in spectra of all the electrodes belonged to PTFE binder at 1215 and 1155 cm^{-1} . Due to low resolution of spectra of *ex situ* electrodes, *operando* characterization was employed in the next step. The first cycle gives a relatively low signal due to low capacity utilization (Figure S12). However, a broad peak decreased at approximately 1650 cm^{-1} during the first cycle coupled with the formation of two very strong peaks at around

1550 and 1300 cm^{-1} can be observed at the end of cycle, which points to the change of IR active bands upon interaction with Al electrolyte. More information can be collected from later cycles. In the 19th cycle, capacity utilization is above 50% of theoretical, which significantly improves the noise to signal ratio (Figure 3). During the discharge, the most significant decrease can be observed at 1548 and 1299 cm^{-1} . These peaks are formed as a result of interaction between pPQ and Al electrolyte species that was observed in the first cycle. Additionally, a decrease of very broad carbonyl peak at 1670 cm^{-1} and a formation of new peaks at 1604 , 1482 , and 1363 cm^{-1} is observed. Among those, the latter corresponds to fully discharged pPQ, while the peak at 1482 cm^{-1} can be attributed to the radical anion [24] pointing to incomplete discharge to radical anion consistent with incomplete capacity utilization of PQ.

To determine the electroactive species involved in the cell reaction, XPS was performed on the *ex situ* electrodes. The spectra were plotted (Figure 4) after energy calibration with respect to the peak assigned to C-C_{sp^2} (details in the SI). The O 1s spectrum of the pristine pPQ is dominated

FIGURE 3: (a) Electrochemical mechanism of pPQ cathode. (b) Subtracted spectra of pPQ electrode during *operando* ATR-IR characterization at different points during 19th cycle (spectra at the start of the cycle are subtracted from each subsequent spectra) (c) and 19th galvanostatic cycle.

FIGURE 4: XPS spectra for O 1s (a), Al 2p (b), and Cl 2p (c) of pristine (top), discharged (middle), and charged (bottom) *ex situ* pPQ electrodes. Black hollow dots are measured spectra; blue, red, and turquoise lines are fitted peaks; green lines are fitted backgrounds; and black lines are the sum of the fits.

by a peak at 531.7 eV, which is assigned to C=O in the carbonyl group, and has smaller peaks at 532.7 eV and 534.0 eV, assigned to C-O and C-OH, respectively [30]. After discharge, the peak corresponding to C=O is reduced, and the peak corresponding to C-O is increased, as was also found in ATR-IR. Similar shifts have been related to the formation of C-O-Al complexes from carbonyl groups [20, 30]. After the charge, the peak assigned to C=O is increased and to C-O is reduced. Although the relative intensity of C=O does not return to that of the pristine electrode, it is similar for the charged electrode compared to an electrode soaked in electrolyte and washed (Figure S13), confirming the

reversibility of the electrochemical reaction but also the strong interaction between the pPQ and the electrolyte observed during the initial cycle of *operando* ATR-IR. The Al 2p spectra reveal the increased intensity after discharge and reduced intensity after the charge of the peak at 75.0 eV. The Cl 2p spectra reveal a similar increase upon discharge and reduction upon the charge, with the position of the Cl 2p_{3/2} peak at 198.8 eV. The peak positions of Al and Cl are similar to reported values for PQ with PVDF-binder reported in the literature [21]. The pristine electrode is found to have small amounts of remaining chloride at 198.3 eV and at 200.1 eV, likely residual Cl-species from the

FIGURE 5: 2D ^{27}Al 3QMAS spectra of (a) soaked and washed, (b) charged, and (c) discharged pPQ electrodes. CS and QIS denote the chemical shift and the quadrupolar induced shift axes, respectively. Red solid lines denote quadrupolar induced shifts for the selected Al sites, and dotted lines are the corresponding isotropic chemical shifts. Top and right spectra are the sum of the direct and indirect dimensions, respectively.

synthesis of the pPQ. After discharge, a peak appears in the N 1s spectra (Figure S14). However, in similarity with literature [10], the at% of N is significantly lower than for Al, so that EMIM^+ is to a minor extent involved as charge carrier. Overall, the spectra from XPS indicate that the major electrochemical reaction involves chloroaluminate species interacting with reduced carbonyl group in pPQ during discharge.

Chloroaluminate speciation was investigated using XPS (Table S2 and S3) and SEM-EDS (Table S4) on *ex situ* electrodes. When corrected for the residual Cl observed in the pristine electrode, the obtained Cl:Al-ratios in the discharged electrodes are 0.86 in XPS and 0.93 in SEM-EDS. Employing additional background subtraction from charged electrodes, which considers electrolyte decomposition products and incomplete electrode washing, results in even lower Cl/Al ratios of 0.77 and 0.64, in XPS and EDS, respectively. Both pointing towards dominant contribution of AlCl_2^{2+} species, as observed in our previous work [12, 20]. The nature of chloroaluminium species that are predominantly incorporated in the pPQ electrodes during the discharge was studied by the ^{27}Al solid-state nuclear magnetic resonance (NMR). Two-dimensional (2D) triple-quantum magic angle spinning (3QMAS) spectra were recorded to differentiate among different quadrupole-broadened contributions. Several ^{27}Al sites were resolved along the isotropic dimension of the sheared 2D spectra, and their anisotropic parts spreading along direct dimension were analyzed to extract the isotropic chemical shifts [31]. Soaking a fresh electrode in electrolyte and washing it with THF prior the NMR measurements confirmed its porous nature being able to permanently detain a portion of AlCl_4^- and Al_2Cl_7^- (narrow peak at 103 ppm and a broad shoulder at about 97 ppm, respectively) in the interstices of the electrode (Figure 5(a)). After several charge-discharge cycles, the amount of the encapsulated electrolyte reached a plateau, but there still was a persistent difference in the number of 4-coordinated and 5-coordinated aluminum sites of the

charged and discharged electrode (Figures 5(b) and 5(c)). The assignment of these new contributions that appeared during the discharging was not straightforward. The relevant solid-state NMR literature on chloroaluminates is scarce, and the solution-state ^{27}Al NMR shifts do not necessarily match the shifts observed in solid-state due to possibly different quadrupole values contributing to the observed isotropic shifts in solutions, but the downfield shift with an increasing x in $\text{AlCl}_x\text{L}_{4-x}$ complexes is expected (L as oxygen donor) [32]. To determine which chloroaluminium species are incorporated during discharging, the spectra of the fresh, charged, and discharged electrodes were compared to the spectra of the three discharge analogues of PQ monomers (Figure S15). The major contribution that appears at about 90 ppm in the spectrum of discharged electrode and also in the spectrum of PQ-AlCl analogue can be assigned to tetracoordinated AlCl_2^{2+} species. The aluminum of the AlCl_2^{2+} complex is likely coordinated with three oxygen atoms of PQ and/or molecules of THF (introduced with washing). Another peak at 52 ppm can be ascribed to pentacoordinated AlCl_2^{2+} species and a narrow peak at 69 ppm to neutral AlCl_3 moieties, but the intensity of the latter is rather low, and it was absent in the spectrum of PQ-AlCl. Apart from the tetrahedral and octahedral sites of electrolyte, the spectra of PQ- 2AlCl_2 and PQ- 3Al_2 were much different from the spectrum of the electrode; thus, AlCl_2^{2+} (101 ppm) and Al^{3+} (<40 ppm) species are likely not present in the discharged electrode.

4. Conclusions

Practical energy densities of the future Al batteries will depend greatly on the type of electroactive species that are utilized. In this work, we studied the electrochemical mechanism of PQ-based compounds. Through application of variety of different *ex situ* and *operando* IR techniques coupled with synthesis of discharge analogues, it was successfully shown that PQ undergoes a two-electron reduction

and not one-electron reduction as previously claimed. Complete insolubility of the cross-coupled polymer enabled us to determine the active chloroaluminium species in discharged *ex situ* cathodes, which are predominately AlCl_2^+ as determined by XPS, SEM EDS and NMR. This leads to the theoretical energy density of 207 Wh/kg, which makes such Al-metal organic battery promising technology for stationary energy storage. PQ-based polymer also shows among the best capacity retention for organic cathodes applied to Al battery system with an average capacity fade of 0.025 mAh/g per cycle. Full capacity utilization of polymer and rate capability performance optimization still remain an open challenge for future research. Electrochemical mechanism analysis using different complementary analysis techniques paves the way for future mechanism analysis of next generation Al batteries and other post Li-ion technologies.

Data Availability

All the data presented within this paper will be made available upon reasonable request.

Conflicts of Interest

The authors do not declare any conflict of interest.

Authors' Contributions

All the authors participated in the discussion of the results, manuscript preparation, and finalization. J. B. and R. D. devised the concept of the work and finalized the manuscript. J. B. performed *ex situ* IR spectroscopy and SEM-EDS. K. P. synthesized PFQ polymer. U. K. was responsible for electrochemical characterization. A. V. performed *operando* IR spectroscopy. N. L. performed XPS analysis, and A. K. performed SS NMR analysis.

Acknowledgments

The research was supported by the Slovenian Research Agency, ARRS (research projects Z2-1864, N2-0165, and Z2-1863 and research core funding P1-0021 and P2-0393). N. L. acknowledges the support from the Swedish Energy Agency (#50121-1).

Supplementary Materials

Calculations of theoretical capacity. Table S1: washing of pPQ electrodes soaked in Al electrolyte with different solvents. Table S2: atomic ratios obtained by XPS of *ex situ* pPQ electrodes. Table S3: atomic ratios (%) normalized per F content obtained by XPS of *ex situ* pPQ electrodes. Table S4: atomic ratios (%) normalized per F content obtained by SEM-EDS of *ex situ* pPQ electrodes. Figure S1: electrochemical cycling of Printex carbon black electrode with PTFE binder. (a) Capacity and Coulombic efficiency of Printex electrode and (b) selected galvanostatic cycles. Figure S2: comparison of PQ electrode with different binders (PVDF and PTFE). (a) Capacity and Coulombic efficiency of cycling for PVDF- and PTFE-based electrodes and (b) selected gal-

vanostatic cycles. Figure S3: (a) SEM figures of a typical PQ electrode with PTFE binder and (b) with PVDF binder. Figure S4: ATR-IR spectra of PQ electrodes in different states of charge. Figure S5: ATR-IR infrared spectra of discharged PQ analogues. Figure S6: ATR-IR spectrum of pPQ active material. Figure S7: XRD spectrum of pPQ polymer. Figure S8: SEM microscopy of pPQ at different magnifications. Figure S9: discharge capacity and Coulombic efficiency of pPQ electrode with high active material loading (6 mg/cm²). Figure S10: (a) Discharge capacity and Coulombic efficiency of pPQ cathode in urea: $\text{AlCl}_3 = 1.3$ electrolyte during long-term cycling at 0.5C and (b) selected galvanostatic cycles. (c) Discharge capacity and Coulombic efficiency of pPQ cathode test in urea: $\text{AlCl}_3 = 1.3$ electrolyte (0.5C-20C) during rate capability test and (d) selected galvanostatic cycles at specific rates (last cycle at specific rate is displayed). Figure S11: ATR-IR spectra of *ex situ* pPQ electrodes. Figure S12: *operando* ATR-IR of pPQ electrode during first cycle at 0.5C. (a) Subtracted spectra at different points during the cycle and (b) corresponding galvanostatic cycle. Figure S13: XPS spectra for O 1s (a), Al 2p (b), and Cl 2p (c) of pristine, soaked, and soaked and washed *ex situ* pPQ electrodes. Figure S14: XPS spectra for C 1s (a), F 1s (b), S 2p (c), and N 1s of *ex situ* pPQ electrodes. Figure S15: ²⁷Al MAS NMR spectra of (a) pPQ electrodes and (b) discharge analogues of PQ. (c) 2D ²⁷Al 3QMAS spectrum of PQ- AlCl_3 and 2D ²⁷Al 3QMAS spectrum of PQ-2 AlCl_2 . (Supplementary Materials)

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