Water-in-Polymer Salt Electrolyte for Slow Self-Discharge in Organic Batteries

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In electrochemical energy storage devices (ESDs), organic electrolytes are typically used for wide operational potential window, yet they suffer with cost, environmental, flammability issues, and low ionic conductivity when compared with water-based electrolytes. Hence, for large-scale applications that require high power and safety, presently there is no true solution. Though water-based electrolytes have higher ionic conductivities, and are cost-effective and non-flammable, their high self-discharge rate with organic/carbon-based electrodes impedes their commercialization. It is found out that highly concentrated polymer electrolytes on the concept of “water-in-salt electrolyte” lead to extremely low leakage current within the electrochemical stability window (ESW) of water, thus solving the issue of self-discharge in organic/carbon-based ESDs. Herein, potassium polyacrylate (PAAK) is prepared as “water-in-polymer salt electrolyte” (WIPSE) and tested for one of the most abundant wood-based biopolymer lignin and polyimide as positive and negative electrodes, respectively, in both half-cell and full-cell. The device shows an open-circuit voltage drops <0.45 V in 100 h setting a record for organic batteries using aqueous electrolyte. The high ionic conductivity (40–120 mS cm⁻¹) nonflammability of PAAK with high ESW (3.1 V) opens a new direction for truly safe, sustainable, and high power (6.8 kW kg⁻¹) organic ESD manufactured by printing technologies.

1. Introduction

High-performance, sustainable, low-cost, and large-scale energy storage devices are the primary requirement in today’s energy-driven society. In contrast to inorganic material-based batteries, organic batteries can fulfill these demand owing to: 1) the high abundance of their constituting atoms (C, O, S, H, N); 2) the versatility of organic chemical synthesis enabling molecular design; 3) the low-temperature synthetic routes; and 4) the possibility to process from liquid dispersions or solutions. Most of the research has been focused on finding organic devices with energy densities competing with inorganic materials. A little attention has been given on organic batteries with high specific power. Hence, a solution for low-cost, large-scale, safe, and high power organic battery has not yet arrived. Electrolyte is one of the key components in electrochemical charge storage devices, because its properties directly affect their technical specifications, that includes specific energy, specific power, safety, cost, and self-discharge (Figure 1a). As presented in Figure 1a, maximizing the operational voltage limit of electrolyte helps to enhance the specific energy whereas; improving the ionic conductivity of electrolyte can contribute to enhance the specific power.

Aqueous electrolytes typically displayed higher ionic conductivity than organic electrolytes. Therefore, one attractive solution for the safe and sustainable high power organic batteries is to use aqueous electrolyte. However, aqueous organic batteries display a major issue: a high rate of self-discharge due to the higher leakage current. The self-discharge process is a spontaneous discharge occurring in open-circuit condition measured by the decay of potential with time. The fast self-discharge...
issue is so severe that it is often not even reported in the literature. Though in Table 1, we summarize key results from the literatures about self-discharge of organic batteries in aqueous electrolyte with materials such as polythiophene p(g42T-T), poly(benzimidazobenzophenanthroline), poly(3,4-ethylenedioxythiophene) (PEDOT), lignin, and polyantraquinone. We also sum up in Table 1 the performance of organic energy storage devices reported in the literature; where many do not report the self-discharge.

The self-discharge process in energy storage devices can originate from several mechanisms: ohmic leakage, diffusion control, and activation controlled Faradaic processes. Let us remind the key equation describing the time ($t$) evolution of the voltage ($V$) for those processes. First, an ohmic leakage process is characterized by an exponential decay

$$V = V_0 e^{-t/RC}$$  \hspace{1cm} (1)

where $V_0$ is defined as initial potential of charged device, $RC$ is the time constant, $R$ is the leakage resistance, and $C$ is the capacitance. The origins of the ohmic leakage could be, for instance, incomplete sealing or interelectrode contacts. For the self-discharge due to a diffusion controlled processes

$$V = \frac{V_0}{t_{\text{ff}} B \sqrt{t}}$$  \hspace{1cm} (2)

where $B$ is defined as diffusion parameter. If the decay in potential of device is governed by diffusion control processes, then the stored charges will be lost by the diffusion of electrolyte ions in electrical double layer. For activation control process, the change in $V$ with $t$ can be defined by Butler–Volmer (or Tafel) equation as presented in Equation (3).
Table 1. Comparative table presents various organic devices with their maximum specific power and specific energy with self-discharge.

| Positive electrode | Negative electrode | Electrolyte | Specific power [kW kg⁻¹] | Specific energy [Wh kg⁻¹] | Self-discharge rate [mV h⁻¹] | References |
|--------------------|--------------------|-------------|--------------------------|---------------------------|-----------------------------|------------|
| Polythiophene p(g42T-T) | Poly (benzimidazobenzophenanthroline) | 0.4 M Na₂SO₄ | 1.9 | 4.4 | 40 | [44] |
| PANI | Poly (bisethylenedioxythiophene-benzobisthiadazole) (Poly(BEDOT-BBT)) | 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide | 3.8 | 13.2 | – | [45] |
| Graphene/poly(o-methyl aniline) (poly(o-toluidine) (POT)) | Graphene/poly(o-methyl aniline) (poly(o-toluidine) (POT)) | 2 M H₂SO₄ | 5.8 | 59.3 | – | [46] |
| Graphene/PANI | Graphene/PANI | 2 M H₂SO₄ | 4.5 | 52.8 | – | [46] |
| Graphene-poly(o-methoxy aniline) (poly(o-anisidine)) | Graphene-poly(o-methoxy aniline) (poly(o-anisidine)) | 2 M H₂SO₄ | 2.5 | 38.3 | – | [46] |
| PEDOT + Lignin/PAAQ | PAAQ/PEDOT | 0.1 M HClO₄ | 5.6 | 8.2 | 136 | [47] |
| Lignin/reduced graphene oxide | Lignin/reduced graphene oxide | 0.1 M HClO₄ | 40 | 10 | – | [48] |
| PEDOT: PSS-cellulose nanofibrils-alizarin red S | PEDOT: PSS-cellulose nanofibrils-alizarin red S | HClO₄ and hydroxyethyl cellulose gel electrolyte | 0.47 | 2.9 | – | [49] |
| Alizarin/Self-assembled graphene hydrogels | Alizarin/Self-assembled graphene hydrogels | 1 M H₂SO₄ | 0.7 | 18.2 | – | [50] |
| Carbon/1,2-dihydroxybenzenene | Carbon/anthraquinone | 1 M H₂SO₄ | 6.3 | 10 | – | [51] |
| Tetrahydroxy-anthraquinone zeolitic framework | Activated carbon nanosheets | 1 M KOH | 3.7 | 47 | – | [52] |
| Graphene framework | Anthraquinone functionalized graphene framework | 1 M H₂SO₄ | 9.1 | 13.2 | – | [53] |
| Lignin/PEDOT/partially reduced graphite oxide | Lignin/PEDOT/partially reduced graphite oxide | 0.1 M HClO₄ | 1.3³\textsuperscript{,} | 3³\textsuperscript{,} | – | [54]\textsuperscript{,} |
| PEDOT | PEDOT | x-Carrageenan sulfated plant polysaccharide/PANI fiber-based hydrogel | 1.7 | 6.1 | 2352 | [43] |
| C-L | C-PI | PAAK | 6.8 | 16 | 3.6 | Present work |

\(^{a}\)Poly(aminoantraquinone); \(^{b}\)Approximated value extracted from graph; \(^{c}\)Calculated by estimating decay in potential from initial potential and then normalized with time.

\[ V = V_0 - \frac{RT}{\alpha F} \ln \frac{\alpha F_i}{RT C} = \frac{RT}{\alpha F} \left( t + \frac{C K}{i_0} \right) \]  \( (3) \)

where \( R \) the is ideal gas constant, \( F \) is the Faradaic constant, \( \alpha \) is the charge transfer coefficient, \( T \) is the temperature, \( i_0 \) is the exchange current, and \( K \) is the integration constant. This process occurs when the device is overcharged and there exist impurities that can shuttle between the electrodes, thereby resulting in charge transfer reactions which reduce the voltage of device at open-circuit condition.

The improvement in specific power and self-discharge is typically obtained by selecting a proper electrolyte which can have high ionic conductivity, high concentration, and high electrochemical stability window.\(^{[7]}\) Herein, we found out that highly concentrated potassium polyacrylate (PAAK) polymer electrolyte based on the concept of water-in-salt electrolyte (WISE)\(^{[8]}\) leads to extremely low leakage which led to record low rate of self-discharge in aqueous organic batteries. The PAAK electrolyte is nonflammable and possesses a high electrochemical stability window (ESW) (\( \approx 3.1 \text{ V} \)) and high ionic conductivity (74 mS cm\(^{-1} \)). This unique combination of properties makes PAAK a competitive and sustainable electrolyte compared to ionic liquids (ILs) for energy storage devices (Figure 1a). The organic battery was built by using composite organic electrodes made of carbon conductors (C) mixed with redox polymers: the synthetic polyimide (PI) in the C-PI negative electrode and the wood-derived biopolymer lignin (L) (\( < 1 \text{ USD kg}^{-1} \)) in the C-L positive electrode (Scheme S2, Supporting Information). Note that the lignin used in this study is desulfonated lignin (DLS) which was prepared from sulfonated lignin (LS). We believe that
in our water-in-polymer salt electrolyte (WIPSE), only K\textsuperscript{+} ions are mobile whereas PAA\textsuperscript{-} anions are immobile. Therefore, both organic redox polymers (PI at the negative electrode and L at the positive electrode) possess an electrochemical activity involving the systematic release and capture of cations. This device configuration is called the “cationic rocking chair” cell where only cations participate during charge–discharge.\textsuperscript{[9]} After the first cycle of oxidation/reduction of L in the presence of PAAK, protons leave the phenol groups to form phenolate groups balanced with K\textsuperscript{+} cations (Figure S11a, Supporting Information). Later, the redox activity of the L in PAAK mostly involves a two-electron redox process with K\textsuperscript{+} cations transported in and out upon reversibly switching between the phenolate and the quinone form (Figure 1c). PI contains conjugated carbonyl groups that can undergo a reversible two-electron redox reaction through an enolization mechanism (Figure 1c).\textsuperscript{[10]} Hence, with this cationic rocking chair architecture, the electrolyte only needs to transport the K\textsuperscript{+} cations. The build device (C–PI//C–L) in PAAK displays <0.45 V drop in potential in 120 h, 6.8 kW kg\textsuperscript{-1} of specific power, 65% retention in initial capacity, and \approx 100% coulombic efficiency up to 2.5k cycles. Selected self-discharge curves are reported in Figure 1b together with the finding of our study that showed the exceptionally low self-discharge rate of organic battery using WIPSE. In this demonstration, we did not use the high stability window to get high energy, but the low leakage current at reasonable potential to solve the self-discharge issue of aqueous electrolyte with organic electrodes. Our findings can provide a facile pathway to manufacture (by coating/printing techniques) and to assemble a cost-effective, scalable, ecofriendly, nonflammable, high power, and stable organic batteries.

2. Results and Discussion

2.1. Characterization of the PAAK

Different concentrations of PAAK electrolytes were prepared where PAAK was dissolved in 1:1, 1:2, 1:4, and 1:6 PAAK/H\textsubscript{2}O wt-ratio with water, which corresponds to a molar concentration of K\textsuperscript{+} of 4.4, 2.9, 1.8, and 1.3 M, respectively. Figure 2a,b displays the current in linear and log scale to be able to examine low levels of current with these electrolytes by linear scan

![Figure 2](image-url)
voltammetry (LSV) measurements. Redox peaks related to water decomposition are visible on both cathodic (≈−0.80 V) and anodic side (≈+0.35 V) for small PAAK/H2O wt-ratio of 1:6 (brown curve) and 1:4 (blue curve). Since the potential difference of these redox peaks is 1.15 V close to water decomposition potential 1.23 V suggesting that these peaks arise due to the electrolysis of water (see Section S2.3, Supporting Information, for explanation regarding water electrolysis). The electrolyte with 1:2 (pink curve) and 1:1 wt-ratio (green curve) did not show any more these redox peaks (which might be associated with electrolysis water molecules), indicating that these faradic leakage currents are strongly reduced. On anodic scans, an exponential increase in current is observed after +1.5 V versus Ag/AgCl, while the increase starts after −1.6 V versus Ag/AgCl (Figure 2a) on cathodic scans and the estimated ESW, of an electrolyte is usually defined as potential range where no significant electrochemical oxidation and reduction of either solvent or ionically conductive salt occurs,[11] of PAAK was found to be 3.1 V. The limits at extreme potentials are due to the reactions such as oxygen evolution reaction (OER) or hydrogen evolution reaction (HER). For the sake of comparison, the LSV of a representative IL, 1-ethyl-3-methylimidazolium ethyl sulfate (EMIES), is plotted in the same graph (black curve). We observed that the water-based PAAK has higher level of leakage current than the EMIES. Outside this work, we are investigating the origins of this current (capacitive, double layer modification, faradaic) with the goal to design WIPSE having low leakage current. Herein, the ESW of PAAK was estimated by LSV methods which is not the most accurate method to determine the ESW,[12a] however, it is sufficient to reveal the lower leakage current in highly concentrated PAAK electrolytes. In future, further efforts are on the way to determine with higher level of accuracy the ESW of electrolytes by chronoamperometric methods and/or using microelectrodes.

The ionic conductivity of PAAK was measured in a two-electrode cell by electrochemical impedance spectroscopy (EIS) (Section S2.5, Supporting Information). The Bode plot in Figure S4a, Supporting Information, displays conveniently that the impedance has a pure resistive behavior at high frequency (≈1 MHz) when the phase angle is zero. Hence, the Nyquist plot (Figure S4b, Supporting Information) reveals directly the total resistive component $R$. To estimate the contact resistance, we used the transfer line method by measuring EIS for five varying lengths between the two electrodes (Figure S4c, Supporting Information). After extracting the contact resistance about 0.5 ohm, the bulk conductivity was calculated using $\sigma = d/ (R \times A)$, where $d$, $R$, and $A$ are the distance between the electrodes, real part of the impedance at zero phase angle, and cross-sectional area of the electrode, respectively. The ionic conductivity of PAAK (at room temperature) was estimated to be $74 \pm 3.1$ mS cm$^{-1}$. The conductivity is largely dominated by the mobile $K^+$, while the contribution of the protons and the immobile polyanions PAA$^-$ can be neglected. In our case, PAAK is in concentrated solutions with a concentration in monomer units from 4.4 M (water:PAAK = 1:1), 3 M (2:1), 1.8 M (4:1) to 1.3 M (6:1). The ionic conductivity of PAAK electrolytes increases linearly with the cation concentration from 45 mS cm$^{-1}$ for $C_{K^+} = 1.3$ M to 122 mS cm$^{-1}$ for $C_{K^+} = 4.4$ M at room temperature (Figure 2c), which suggests that most cations participate to the conduction and few neutral ion pairs are formed.

Finally, we compared the flammability of PAAK with EMIES. A glass fiber wool was loaded with the electrolyte and then a flame from a Bunsen was burning the sample for 10 s and turned off (Figure 2d). From that time, we measured the sustained period of burning for a certain weight of electrolyte, to define the self-extinguishing time (SET). For PAAK, the flame is extinguished simultaneously to the Bunsen’s flame, so the SET is 0 s g$^{-1}$ and it is classified as truly nonflammable. For EMIES, the flame continues to grow and burn even after 59 s, indicating that it is combustible.

2.2. The State of Water in WIPSEs

To shed light on the superior ionic conductivity of our WIPSE (40–120 mS cm$^{-1}$) compared to the molecular WISEs (1–10 mS cm$^{-1}$), we described more in depth the polymer electrolyte solutions. In diluted polymer electrolyte solutions, the entropy drives the cations away from the polyanions such that both are preferentially fully solvated (Figure 3a). In a good solvent, a strongly charged polymer chain is stretched due to the electrostatic repulsion between the charged monomer units. When increasing the polymer electrolyte concentration, it is preferable for some cations to condense along the polyanionic chains,[13] thus forming kind of solvated ion pairs (dipoles), which decrease the electrostatic repulsion within the chains and reduce the end-to-end chain distance (Figure 3b).[14] The ion condensation effectively decreases the charge density of the chains and affects its morphology by making noncollapsed coils. Above a critical concentration ($>10^{-2}$ g L$^{-1}$),[15] polymer electrolyte chains in semidilute solutions overlap become entangled and form like a 3D-mesh described as a transient network structure (Figure 3c).[16] Both small angle neutron scattering[17] and small angle X-ray scattering[18] demonstrate the existence of a scattering peak associated to an average distance between the chains (typically several tens of nanometers). For our highly concentrated solution of PAAK, the viscosity increases superlinearly with the concentration (Figure S5, Supporting Information) and supports the creation of a network of entangled polymer chains.[19] Recent theoretical efforts have been toward a description of the phase diagram for polymer electrolyte solutions, including the dilute-to-semidilute crossover strongly dependent on the degree of polymerization but typically visible in the concentration range of $[10^{-2}–1]$ m.[20] In that concentration range, the ionic conductivity $\sigma$ scales linearly with the concentration as expected from a constant ionic mobility with concentration $[1.2$ mS cm$^{-1}$ for 0.04 M of a fully sulfonated polymer$][18]$.

For the semidilute-to-concentrated crossover ($C > 1$ M), theoretical predictions suggested the close distance between the polymer chains (<1 nm$^{-1}$) could result in a possible attraction potential between the screened polymer electrolyte chains.[21] The notions of free and condensed ions should totally collapse at these high concentrations. Interestingly, this range of concentration is experimentally achievable with PAAK due to its high charge density, chain flexibility, and hydrophilicity. The absence of light scattering in the visible in those transparent...
solutions indicates no strong aggregation between the polymer chains, but possibly a water-rich nanophase ensuring the fluidity between the polymer electrolyte chains (Figure 3d). Note that water in an IL is found to phase separate in nanodomains,[22] while in water-in-molecular salt (e.g., LiTFSI), TFSI⁻ anions form a 3D network with water nanophases (1–2 nm).[23] From those observations, we propose that the ion transport involves partially solvated cations that move by hopping-like transport, i.e., without their solvation shell, in an electrostatic landscape created by the polyanions screened by water aggregates (Figure 3e).

The hypothesis of water-rich nanophases between the partially screened polyanions is confirmed by Fourier transform infrared spectroscopy (FTIR). Indeed, water molecules in the liquid state are characterized by two stretching modes: one antisymmetric mode (band 1 in Figure 3g) at 3440 cm⁻¹ and one symmetric at ≈3250 cm⁻¹ (band 2), as well as a bending mode at ≈1650 cm⁻¹.[24] The contribution at wavenumber ≈3450 cm⁻¹ is strongly involved in the hydrogen-bonded water molecules.[25] The vibrational modes of PAAK is featured by a C–H stretching at ≈3000 cm⁻¹ (band 3 in Figure 3g) and the asymmetric stretching mode for COO⁻ at ≈1550 cm⁻¹.[26] To investigate the state of water, ATR-FTIR spectra were recorded for different concentration of PAAK (Figure 3f). The broadband centered at ≈3320 cm⁻¹ corresponds to O–H stretching bands and a sharp band at ≈1640 cm⁻¹ associated with O–H bending band. The FTIR spectra of PAAK powder (Figure 3f and Figure S6, Supporting Information) display clear band at ≈2930 cm⁻¹ corresponding to −C–H stretching mode (band 3 in Figure 3g) whereas, band at ≈1695 cm⁻¹ arises due to the −C=O from carboxylate (band 4 in Figure 3g). In highly concentrated PAAK, we do not observe such drastic decrease of the contribution at ≈3440 cm⁻¹, suggesting that H-bonds are still dominant for water in electrolyte despite the high concentration. On the contrary, for some in WISEs devoid of free water molecules, the H-bonds between water molecules disappear because the water molecules interact with the ions and are featured by a dramatic drop in the intensity of the stretching mode at 3450 cm⁻¹, related to a shift of the vibrational modes toward high wave numbers (≈3550 and ≈3610 cm⁻¹).[27] For the WIPSE, neither the shift in band position nor the dramatic change in intensity was observed for O–H bending mode, thus indicating that water–water interactions are still dominant and reinforcing the hypothesis of the existence of water nanoclusters. After spectral deconvolution, the integrated intensity ratio between stretching (I₁ + I₂) and bending modes (I₅) was calculated to be (I₁ + I₂)/I₅ = 2.81, 2.83, 2.98, and 3.03 for PAAK 1:1, PAAK, PAAK 1:4, and PAAK 1:6 polymer electrolytes, respectively, while the same spectral ratio is higher for pure water (≈3.22) (Figure 3h). Hence, even if water molecules do not display major shift in their vibration mode, their vibrational cross section is modified due to their confinement within the mesh of the entangled PAAK chains, constituting a different environment than pure water.

2.3. Organic Battery Based on WIPSE

We now turn to the demonstration of an all organic-based battery that has a slow self-discharge in PAAK polymer electrolyte. Two
low-cost organic polymers, biopolymer lignin and aromatic polymer, were chosen to investigate the self-discharge behavior for the sustainable organic battery. The redox potential of those two polymers leads to a voltage about 1.1–1.2 V at the edge of the thermodynamic stability window of water. The low leakage current observed in Figure 2a,b with PAAK indicates a slow kinetic of the water electrolysis and thus an enhanced stability of the electrolyte-carbon collector contacts for this potential range. These redox polymers were mixed with C nanoparticles in a 50/50 wt% ratio to obtain the nanocomposite electrodes C-L and C-PI. C is introduced to bring the electrical conductivity to the nonconducting polymers. Note that as lignin is more electrically insulating than the aromatic polymer, we needed to use ball-milling to break the carbon conductors in even smaller pieces and make an intimate interface with the lignin. The cyclic voltammetry (CV) of the electrodes normalized by mass is presented in Figure 4a. First, these CVs suggest a stable potential window from −0.2 to 0.7 V versus Ag/AgCl for the C-L electrode and from 0 to −1 V versus Ag/AgCl for the C-PI electrode, thus motivating the choice of C-L as positive electrode and C-PI as negative electrode in the assembled battery. C-L and C-PI nanocomposite electrodes tested in half-cell configuration (see Section S3, Supporting Information) and showed a specific capacity of 17.1 and 99 mAh g⁻¹, respectively, at 1 A g⁻¹ of current rate. Before assembling the device, it is crucial to perform mass balance of the C-L with C-PI electrodes. The mass ratio between the electrodes was found to be ≈6:1 for C-L and C-PI while considering their charge density. A device was then finally constructed using C-L, C-PI electrodes with PAAK electrolyte. The voltammograms of the device (Figure 4b) show one broad oxidation and one broad reduction peak, where the former one is attributed to the oxidation of C–C–OK (or C–C–CO⁻K⁺) to C–C=CO in the chemical structure of the polymers (Figure S11a and S14a, Supporting Information). The peak currents increase with scan rates, which suggests that the ionic and electronic charge transport, along with the interfacial redox processes, are rapid. At 0.1 A g⁻¹ current rate, the discharge curve shows a plateau within the range from 1.1 to 0.7 V and then the potential drops relatively fast (Figure 4c). The device shows a maximum specific capacity of 19 mAh g⁻¹ (∼40 mAh g⁻¹ based on only polymer weights), at 5 C rate, which decreases to 11.6 mAh g⁻¹ (∼39% loss in specific capacity) as the current increases about 80 times (400 C rate) (Figure 4c). These results demonstrate a rather good rate capability for an all-organic battery, here based on PAAK. The device delivers a maximum specific energy of ≈16 Wh kg⁻¹ (26.6 Wh kg⁻¹ based on polymer weights), at a specific power of 85 W kg⁻¹, which then reduces to 9.9 Wh kg⁻¹ at a high specific power of 6.8 kW kg⁻¹ (∼10 kW kg⁻¹ based on only polymer weights) as estimated by the Ragone plot of Figure 4d. The small decay of the specific energy versus specific power indicates that all the processes possess fast kinetics (electron transfer of the redox reaction, as well as electronic and ionic transport). Moreover, the cyclability of the assembled device was tested up to 2500 cycles, which retained 65% of its initial capacity (Figure 4e). Subsequently, the coulombic efficiency was found to be 99% after 2500 cycles, indicating a good long-term stability of the device in PAAK (Figure 4e).
All the previous performances are not unique for organic batteries, but there is one performance which is unique in this PAAK-based organic battery: its self-discharge behavior. It is a well-known fact among specialist that nobody can achieve an extremely slow self-discharge by combining an aqueous electrolyte with organic electrodes; this is the reason in many articles it is even omitted (see Table 1). But we discover here that the self-discharge characteristics of this organic battery constitute a breakthrough in the field of organic energy storage. As presented in Figure 1b, we display the superior results (pink and blue curves) in voltage and self-discharge time obtained with the WIPSE for our organic battery compared to the other representative devices based on organic (e.g., PPy, PEDOT, 2-aminoanthraquinone, etc.) and carbon electrodes in aqueous electrolyte. Herein, two devices were built where device 1 (blue curve) was charged first at 0.1 A g⁻¹ current rate up to 1.7 V, while device 2 (pink curve) was charged to 1.3 V. We find that in device 1 the cell voltage drops to 0.67 V from 1.1 V (corresponding to discharge voltage plateau) in 5 days, whereas in the device 2 open circuit voltage (OCV) reaches to 0.59 V from 1 V in 4 days (Figure S20, Supporting Information). The half voltage decay time (calculated from maximum charged voltage 1.7 V) was also calculated for both devices which was found to be 28.8 h for device 1 and 76.8 h for device 2 (Figure S20, Supporting Information). These results demonstrate that the PAAK provides exceptional slow self-discharge rate, and it is now possible to truly speak about low-cost, high power, and inflammable organic battery for damping fast power fluctuation in large-scale energy storage.

To understand the origin of the self-discharge, we attempted to fit the time evolution of the voltage with one equation at a time: Equation (1) for ohmic leakage and Equation (2) for diffusion control process (Figure S21, Supporting Information), but none could fit the result. Hence, the self-discharge in our organic batteries is likely due to the several processes taking place simultaneously. The self-discharge curve presented in Figure 4f was fitted using Equation (4) \[ V = A - B\sqrt{t} - P\ln(t + Q) \] where \( A, P, \) and \( Q \) are parameters related to the Faradaic processes.\(^{[12]}\) For our device, the self-discharge curve fitted perfectly using Equation (4) suggests that the decay in voltage of device is governed by diffusion controlled and activation controlled Faradaic process (Figure S22, Supporting Information). Moreover, this result also indicates that ohmic leakage can be neglected. The obtained values of parameters \( A, B, P, \) and \( Q \) are presented in Table S4, Supporting Information. For our case, the value of diffusion parameter \( B \) was estimated to be \( 2.1 \times 10^{-4} \text{V s}^{-1/2} \) which is lower than the values reported in the literature for different electrochemical devices.\(^{[6,29]}\) This signifies that the diffusion of ions from double layer is slow and results in a slow loss of charges and hence low self-discharge rate. The diffusion parameter \( D \) depends on the excess ionic concentration \( (c_{\text{EIC}}) \) in the double layer, the interfacial series capacitance per unit area of both electrodes \( C \) and the ionic diffusion coefficient \( D \) (Equation (5)).\(^{[6a,b]}\)

\[
B = \frac{c_{\text{EIC}} \sqrt{D}}{C} \quad \text{(5)}
\]

Self-discharge of device C–P1//C–L was also performed at various temperatures as presented in the inset of Figure 4f. The rate of decay in voltage increased with temperature. In 24 h, the OCV reduced to 0.88, 0.85, 0.79, and 0.61 V from 1.1 V at 12, 24, 36, and 50 °C. This could be attributed to the increase in \( B \) with temperature and we believe this is mostly due to the change in ionic diffusion coefficient \( D \) (Figure 5a). Indeed, the ionic diffusion in highly concentrated electrolyte can be thermally activated \(^{[30]}\) and follow an Arrhenius behavior \( D = D_0 \exp (-E_p/kT) \). This is corroborating with our observation because there is indeed a linear relationship between \( \ln B \) versus \( 1/kT \) (Figure 5b). Irrespective of temperature, all the devices tested in WIPSE displayed exceptionally slow self-discharge which can be credited to the reduction in diffusion parameter value. Based on these findings we believe that “WIPSEs” can be utilized to suppress the self-discharge associated with carbon/organic electrochemical energy storage devices.

### 2.4. Discussion

A first point to discuss is to localize this finding in the research field of polymer electrolyte. Our goal is not to compare to record high values for polymer electrolyte system, but to pinpoint our finding with the past major research trends for polymer...
electrolytes. Two major families of polymer electrolytes have been abundantly studied for energy storage applications. A first benchmark system is the polyethylene oxide (PEO) loaded with a salt to form a solid-state electrolyte for metal-ion battery. This strategy provides high ESW but suffers with poor ionic conductivity typically below 0.1 mS cm\(^{-1}\) at room temperature.\(^{[13]}\) Another family of polymer electrolyte is the gel electrolyte in which, for instance, a certain amount of polyvinyl alcohol (PVA) (10–20 wt%) forms a polymer matrix in that a large amount of liquid solvent and salt is hold in a gel/solid state. The use of water as solvent is the most popular way to reach high ionic conductivity (\(\approx 20\) mS cm\(^{-1}\)) but these hydrogels have the issue to exhibit a low ESW due to water electrolys. The presence of significant leakage current in the 1.23 V range is seen as an issue for self-discharge. In contrary to these families of polymer electrolytes, the new family of “WIPSE,” here illustrated with PAAK, presents a unique combination of properties: first, a high ionic conductivity 120 mS cm\(^{-1}\) is one of highest values achieved for polymer electrolytes. The high concentration of the polymer is obtained because of its high polymer chain flexibility and ability to form H-bonds. As the polymer PAAK is also the salt, those gels possess a very high ionic concentration (2–4 M) helping to achieve a good ionic conductivity. Second, the WIPSEs provide a low electrolysis leakage current in a 2 V range despite the presence of water, which is beneficial to decrease the self-discharge rate, as well as a high ESW to increase the energy storage ability of a device. Third, this type of electrolyte is close to neutral in pH, thus preventing issue of corrosion with metal collectors. Fourth, its nonflammability and cost-effectiveness (price of polyacrylic acid is 1 USD kg\(^{-1}\)) are important to provide a true sustainable solution for large-scale energy and power storage.

There are number of established battery technologies that can provide high specific energy and cyclic stability. Though Li-ion batteries are at the forefront in terms of performance, yet the sustainability of all battery components has been overlooked.\(^{[13]}\) Hence, a second point to discuss is about the multiple sustainability features of the organic battery concept proposed. First, the organic battery proposed has an absence of critical raw material because only organic and carbon materials are used, which makes the recyclability scheme simple as these are all carbon-based materials. Second, the environmental aspect is related both on the easy scaling up of the redox polymers via wet chemistry (low temperature, low energy intensive process), as well as the water-based manufacturing process of the battery (no nasty volatile solvent during the coating of the slurry for the two electrodes and the electrolytes); and finally, use of the biopolymer lignin as true storage material is unique. Third, the economical sustainability is not only related to the cost of the material chosen but the lifetime and cyclability of the battery. Our choice of materials (PAAK, PI, lignin, and carbon black) leads to one of the cheapest batteries, such that including the obtained lifetime performance, the estimated price of the battery is 0.8 USD kWh\(^{-1}\) per cycle (including all the components) majorly dominated by the price of PI which could be further reduced to 0.26 USD kWh\(^{-1}\) per cycle by choosing less expensive PI.

The last point that should be discussed is the performance of the organic battery proposed compared to other energy storage technologies. The specific energy is larger than supercapacitors and redox flow batteries; but much lower than metal-ion batteries or metal-air batteries. The performance in terms of specific energy of C–I and C–PI based device can be further improved by introducing conducting polymer\(^{[14]}\) instead of carbon conductors, by functionalizing the lignin with a higher density of catechol groups such as in polycathecols\(^{[15]}\) or by reducing the monomer mass of the PI such as in a pyromellitic polyimide.\(^{[16]}\) One feature of this combination of organic redox polymer is the potential ability to use its high power (6.8 kWh kg\(^{-1}\)). Although we have not included the weight of the collector, we observe that the electrode materials and the electrolyte enable specific power higher than most of Li-ion batteries and redox flow batteries.\(^{[17]}\) Hence, our combination of materials, including fast redox organic quinones of PI and lignin, high conductivity PAAK electrolyte, appears to offer a unique opportunity for large-scale energy storage devices to fulfill the high power requirement for grid applications. The safety issue so crucial for large-scale storage is fulfilled with the WIPSE strategy because of the use of water. The big bottleneck of water electrolyte for cheap and green organic redox materials for safe large-scale energy storage was the self-discharge, which is today solved in this present article using WIPSEs. Therefore, we dare to claim that the device proposed provides a unique solution for economical, sustainable, safe, and high power large-scale energy storage devices.

3. Conclusion

The research on large-scale, stationary, and electrochemical energy storage devices has focused on the use of sustainable materials combining safety, low cost, and high specific energy. Today, the design of large-scale energy storage for damping power fluctuations on the grid is not only requiring large energy storage device functioning at low power (e.g., redox flow batteries), but also large devices that can damp fast and high fluctuation of power. In this work, we combine nonflammable WIPSE and low-cost biopolymer lignin-based organic electrodes to propose a solution for low-cost, large-scale, safe, and high power energy storage device.

Here, we present PAAK as WIPSE that possess a unique combination of features difficult to obtain with organic electrolyte: low-cost, environmental benign, high voltage operation with an ESW 3.1 V, nonflammable (SET = 0 s g\(^{-1}\)), and high ionic conductivity (up to 120 mS cm\(^{-1}\) at 20 °C). Interestingly, the viscosity of the polymer electrolyte could be tuned over four orders of magnitude while keeping the ionic conductivity of the same order of magnitude (40–120 mS cm\(^{-1}\)), which has strong implication for the flexibility for manufacturing the energy storage devices, for instance, by using low-cost printing/coating technologies. We found out from ATR-FTIR that in concentrated solution of PAAK cations transported without their solvent shell but rather through hopping transport in a 3D-mesh of polyanions separated by water nanoaggregates. The remarkable low leakage current of PAAK at typical potential for water electrolysis solves the general issue of drastic self-discharge in aqueous organic batteries. We validate this concept by using the “WIPSE” with sustainable organic redox polymer electrodes (lignin and polyimide) and use the exceptional high ionic conductivities to fabricate high power organic battery (Table 1). The devices displayed slow self-discharge rate retaining the energy for several days, which
is, to the best of our knowledge, the world record for self-discharge behavior among organic energy storage based on aqueous electrolytes. This breakthrough opens a new avenue for nonflammable, large-scale, low-cost, and high-power organic energy storage devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

biopolymers, lignin, organic battery, polymer batteries, polymer electrolytes, self-discharge, water in salt

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