Self-Discharge in Batteries Based on Lignin and Water-in-Polymer Salt Electrolyte

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Lignin, the most abundant biopolymer on earth, has been explored as an electroactive material in battery applications. One essential feature for such lignin-based batteries to reach successful usage and implementation, e.g., large-scale stationary grid applications, is to have slow self-discharge characteristics on top of the essential safety and life-cycle properties. Water-in-polymer salt electrolytes (WIPSEs) have been demonstrated as an attractive route to solve this issue; however, little has been done to understand the fundamentals of actual self-discharge mechanisms. Herein, the impact of some critical chemical and physical parameters (pH, dissolved oxygen, viscosity, and cutoff potential) on self-discharge of batteries based on WIPSE and lignin has been investigated. The pH range is crucial as there is an interplay between long-term stability and high energy density. Indeed, lignin derivatives typically store relatively more charge in acidic media but later promote corrosion affecting device stability. A robust and high-performing organic battery, incorporating potassium polyacrylate as WIPSE, is demonstrated, which expresses good self-discharge behavior for a broad range of pH and with little impact on the atmosphere used for manufacturing. It is believed that the investigation will provide critical insights to the research community to promote the advancement of printed large-scale energy storage devices.

1. Introduction

Large-scale stationary batteries are researched and explored to increase the capacity at power peaks and to avoid oversizing electric grid. Especially, this is a great challenge as more and more renewable energy is deployed in our society. Various chemistries, such as Na–S and Li-ion, and different battery architectures, such as solid state or redox flow batteries, are considered. However, achieving high specific energy is not the primary objective in these types of batteries. Instead, the cost/kWh/cycle as well as the recyclability and safety are the controlling specifications for their successful implementations. Hence, it is expected that Li-ion batteries, although appropriate for portable and mobile applications, are not the ideal choice for stationary applications because the cost of electrode materials and flammability of the electrolyte define critical hurdles. The use of aqueous electrolyte is attractive for large-scale batteries because of their nonflammability. This is exemplified by the success in the deployment of large-scale aqueous redox flow batteries. Seeking abundant and green materials for sustainable batteries is important to reduce the overall cost and enables easy recycling protocols for the electrode materials. In that context, several years ago, scientists have demonstrated the use of the biopolymer lignin (representing 20%-30% of the matter of plants) which has ample aromatic moieties as green and low-cost electrode materials in batteries. Since that early finding, several efforts have been done to explore the potential of this idea. Lignin, an electrical insulator, needs to be composited with conductors at the molecular level to access the electrochemical activity of its aromatic groups. Lignin has been integrated with carbon nanotubes, conducting polymers, carbon black, graphene, and graphite to form conductive nanocomposite electrodes. Also, various battery concepts have been demonstrated based on the material, such as Li-ion based lignin–inorganic batteries including an organic electrolyte and organic batteries operating in an aqueous electrolyte.

Regardless the energy stored, or power provided, practical applications of lignin-based batteries must address the self-discharge issue. Self-discharge is the spontaneous voltage...
decay process running over time of electrochemical energy storage devices at open-circuit conditions. The decay in voltage of a device is often ascribed to an ohmic leakage, a charge redistribution, and/or parasitic faradaic processes in a charged device at a high energy state. Leakage currents may also originate from incomplete sealing or interelectrode contacts. Charge redistribution can also take place when a device is overcharged, and the voltage across the double layer can drop until the overvoltage ($\eta$) is zero through overcharging currents. Any impurity in the electrolyte which is redox active at operable voltages of device can lead to rapid drop in voltage in the device, for instance, $\text{O}_2/\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couples. Efforts have been made to suppress the self-discharge rate by modifying the electrodes, the separator, or the electrolyte. However, due to the complexity of the mechanisms involved in self-discharge, the self-discharge is often seen as a black box and is a grand challenge when optimizing a battery technology.

A recent successful approach for lignin-based batteries is the architecture with lignin mixed with conductive carbon (hereafter termed as L–C) as the positive electrode and polyimide/carbon (hereafter termed as P–C) as negative electrode (Figure 1a). The materials chosen are among the most inexpensive organic electroactive materials. The cationic rocking chair cell (Figure 1c) stores energy by using mobile cations to compensate the negative charges carried by the two redox polymers (Figure 1b). The charge and discharge are accompanied by the oxidation and reduction of the complementary redox polymers and by the transport of cations moving back and forth between the electrodes (Figure 1c). The redox chemistry of lignin requires two electrons for oxidation and reduction accompanied by $2\text{K}^+$ cations transported in and out of the organic electrodes. During the first cycle of oxidation and reduction of the L–C electrode, protons leave the phenol groups to form phenolate, which is then balanced by the $\text{K}^+$ counterions present in the electrolyte. In a similar way, P–C also undergoes a two-electron reversible redox reaction through an enolization mechanism owing to the presence of conjugated carbonyl groups. Our investigated battery configuration works according to the “cationic rocking chair” mechanism, where battery operates with an electrolyte that only transports cations. In that context, we have introduced the use of the potassium polyacrylate (PAAK) as a possible water-in-polymer salt electrolyte (WIPSE) with a large difference in diffusion coefficients for the polymeric quasi-immobile anions and the mobile atomic cations.

Our strategy to use WIPSE based on PAAK is not to increase the stability window of the electrolyte to propose high voltage faradic polymers, but rather to achieve low leakage current in the stability window of water to get unprecedented self-discharge characteristics in organic batteries operated in aqueous electrolyte. This new class of electrolytes has also been processed in scalable low-cost manufacturing protocols, such as using printing/coating techniques. This has been possible because the viscosity of PAAK–WIPSE can easily be tuned over four orders of magnitudes without considerably affecting the high ionic conductivity ($\approx 80 \text{mS cm}^{-1}$). This is an advantageous feature while striving for low-cost batteries produced at large scales.

In the present article, we report on the mechanism of self-discharge of this specific organic battery (Figure 1a), and our work is motivated by the true potential for economically viable large-scale storage solutions with anticipated sustainability features. The effect on self-discharge was analyzed by varying several key physicochemical parameters, such as the pH (varies from 2 to 6.2), the concentration of $\text{O}_2$ as impurity, and the impact of charging voltages. Surprisingly, no dramatic change was observed. This leads us to propose that the long-term self-discharge mechanism might be inherent to the redox polymers included at the electrodes. In practice, we also demonstrate that this organic battery is utterly robust and relatively much less expensive to manufacture because production can occur at ambient environments. This is a major advantage to achieve for easy

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**Figure 1.** a) Schematic illustration of the organic battery with L–C as positive and P–C as negative electrode, respectively. b) Typical cyclic voltammetry (CV) curves of the L–C electrode (green) and the P–C electrode (brown) in a three-electrode setup. The two CVs are superposed in the same graph to illustrate the potential of redox activity versus the reference (Ag/AgCl). c) Mechanism of the “cationic rocking chair” organic battery presented here based on lignin with catechol group as redox polymer on the positive L–C electrode and polyimide as redox polymer on the negative P–C electrode. Only cations need to be transported through the electrolyte, thus motivating the use of WIPSE (PAAK).
and large-scale production protocols, which is typically a major hurdle for many other types of batteries.

2. Results

2.1. Effect of pH on the Self-Discharge

In this all-organic battery, polyimide and lignin were selected and mixed with conductive carbon to form the electrodes. We investigated the performance of those aqueous batteries including different WIPSEs by varying the PAA derivative composition. We suspected the reduction of residual protons in the aqueous electrolyte, occurring at the negatively charged electrode, as the major cause of self-discharge. For this reason, the device performances were studied using WIPSE having different pH (Figure 2a,b). The pH of the PAAK electrolyte was altered by introducing varying amount of polyacrylic acid (PAAH). The viscosity of the electrolyte increases upon addition of PAAH as observed by rheological studies (Figure S1, Supporting Information). We tentatively attribute this effect to the increase in the hydrogen bonding between different polymeric chains.[21]

The attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra reveal that the increase of pH by adding KOH in PAAH leads to a disappearance of vibration of the –COOH groups and the presence of new vibrations bands due to PAAK, thus fewer acid groups are able to form H-bonds (Figure S2, Supporting Information; discussed in detail). The CV and galvanostatic discharge profiles show electrochemical activity for all included WIPSEs (Figure 2a,b). Well-defined redox peaks can clearly be seen in the voltammograms (Figure 2a) and galvanostatic discharge profiles exhibit a specific capacity varying between 20 and 34 mAh g\(^{-1}\) for electrolytes with different pH (Figure 2b) without any systematic trend with pH. However, devices including WIPSE with pH 2 and pH 2.8 display the lowest specific capacity, which is attributed to the low electrochemical activity of polyimide in acidic medium.[22]

The self-discharge behavior for the WIPSEs at different pH is presented in Figure 2c. The fast decay, starting from the cutoff voltage of the charging at 1.7 V, is attributed to the absence of redox potential in the battery within the voltage range 1.0–1.7 V. In that potential range, only a small capacitive charge can be stored, and the voltage decay cannot be counted as the intrinsic self-discharge of the actual organic battery. On the contrary, at about 1 V, the charge stored hold by the redox processes of the polymer electrodes; and thus, the true self-discharge process is found below 1 V. Interestingly, we did not observe any dramatic effect of pH on the overall performance of

![Figure 2.](https://www.advancedsciencenews.com/wanted.png)

Figure 2. a) CV of the organic battery for different pH at 50 mV s\(^{-1}\) sweep rate, b) galvanostatic discharge profiles of device at 0.1 Ag\(^{-1}\) current density, c) comparative self-discharge behavior in log scale of devices built using different WIPSEs with cutoff voltage of 1.7 V, and d) values of B (diffusion parameter) for variation in pH.
self-discharge of the devices even up to 3 days, while the activity of the proton in the electrolyte was varied by five orders of magnitude. Hence, we can clearly rule out the reduction of proton at the negatively charged electrode as the main mechanism of self-discharge.

2.2. Fitting the Self-Discharge Curves

Having ruled out the proton reduction, we further analyzed features in the self-discharge curve with the aim to identify other possible mechanisms, such as ohmic leakage, diffusion-controlled processes, and activation-controlled Faradaic processes.

The ohmic leakage of the cell could arise from the interelectrode contacts or incomplete sealing which can be defined by the relationship between cell voltage (V) and time (t) according to

\[ V = V_0 e^{-t/RC} \]  

where \( V_0 \) is defined as the initial potential of the charged device, \( RC \) is the time constant, \( R \) is the leakage resistance, and \( C \) is the capacitance. The self-discharge due to a diffusion-controlled process can be estimated by

\[ V = V_0 - B\sqrt{t} \]  

where \( B \) is the diffusion parameter. For diffusion-controlled processes, stored charges are lost by the diffusion of electrolyte ions in the electrical double layers or by the diffusion of any redox impurity.

If the self-discharge process is governed by the rate of electron transfer involved in a side Faradic reaction, the change in V with t follows the Tafel equation

\[ V = V_0 - \frac{RT}{aF} \ln \frac{\alpha F_i}{aF} - \frac{RT}{aF} \ln \left( t + \frac{CK}{\alpha} \right) \]

where \( R, F, \alpha, T, i_0, \) and \( K \) are ideal gas constant, Faradaic constant, charge transfer coefficient, temperature, exchange current, and integration constant, respectively. An activation-controlled Faradic process occurs often when the device is overcharged, thereby resulting in a spontaneous decline of potential at open-circuit conditions.

To understand the origin of the self-discharge, we attempted to fit the time evolution of the discharge voltage curves with one equation at a time: Equation (1) for ohmic leakage and Equation (2) for diffusion control process (Figure S3 and S4, Supporting Information), but both equations failed in fitting the results for all WIPSEs. This absence of good fitting suggested that the self-discharge process is not only due to ohmic leakage or diffusion-controlled processes but rather that several processes take place concurrently. Therefore, the self-discharge curves were fitted with Equation (4), which includes the contributions from both diffusion-controlled and activation-controlled Faradaic processes.

\[ V = A - B\sqrt{t} - P \ln(t + Q) \]

where \( A, P, \) and \( Q \) are parameters related to Faradaic processes. All the self-discharge curves were successfully fitted using Equation (4) (Figure S5, Supporting Information), suggesting that the self-discharge process in all devices originates from the combination of a diffusion-controlled and an activation-controlled Faradaic process. The estimated \( B \) value was found to be \( \approx 5 \times 10^{-5} \text{V s}^{-1/2} \) for all tested devices. As mentioned, the pH of the electrolyte was altered by adding PAAH in PAAK which also changes the viscosity of electrolytes. Herein, it was observed that \( B \) was not only constant with pH but also independent of the viscosity, which was varied from 500 to 5500 cP (Figure 2d). We now know the proton reduction is not involved but that a Faradic process must be involved to reach a good mathematical fitting. This led us to suspect the reduction of the dissolved oxygen in the electrolyte as a potential parasitic Faradaic current at high potentials.

2.3. Dissolved Oxygen Reduction and Potential Effect

To investigate the effect of dissolved oxygen in the electrolyte on the self-discharge, two O2-free electrolytes were prepared: the first is obtained by purging the prepared PAAK electrolyte with N2; the second by purging water with N2 prior to addition of PAAK salt. The obtained self-discharge profiles displayed no dramatic change in self-discharge rate in comparison with the normal PAAK electrolyte prepared in atmospheric condition (Figure 3a).

As mentioned before, the battery devices display fast decay in the 1.7–1.0 V range. To further analyze the issue of overcharging, the L–C/PAAK/P–C batteries were charged at different voltages (0.9, 1, 1.2, 1.4, and 1.7 V) and then their self-discharge profiles were recorded (Figure 3b). Within 3 days, the devices displayed 54%, 51%, 49%, and 43% decay in voltage when charged up to 1.7, 1.4, 1.2, and 1 V, respectively. However, the device charged up to 0.9 V showed 48% decay in voltage within 3 days. Hence, again those data points reveal two self-discharge mechanisms, one occurring before 0.1 day that is potential dependent and another one after 0.1 day that shows a self-discharge rate being constant with the voltage.

3. Discussion

For the L–C/PAAK/P–C battery here studied, the self-discharge profiles are very similar and can be divided in two regimes: regime 1 with a sharp voltage drop and regime 2 with a slow rate almost appearing as a plateau (Figure 4a). Our experimental investigations reveal that the regime 2, which from an application point of view is the most interesting, is not related to any Faradaic reactions, such as proton or oxygen reduction. We suggest that
the self-discharge mechanism involves the electronic structure of the redox polymer electrodes. Redox active polymers in contact with an electrolyte are known to have a broad Gaussian distribution of levels,[24] The transfer of charges from the collector to the polymer, as well as the transport of charges within the polymer close to the center of the Gaussian distribution, is efficient because there are many localized levels close to each other in energy and in space. On the contrary, the transport of charges

Figure 3. Comparative self-discharge behavior in logarithmic scale of devices built using different WIPSEs with a) effect of removal of oxygen by N₂ purging; b) different cutoff voltage of 1.7 V.

Figure 4. Self-discharge mechanism involves electronic structure of the redox polymer electrodes: a) general two regimes for self-discharge, b) Gaussian distribution of injected charge carriers diffused at lower energy levels, c) comparative self-discharge, and d) CV (at 50 mV s⁻¹) comparison of two cells L–C//PAAK//AC and AC//PAAK//P–C.
at the tails of the Gaussian distribution is often distant in space which limits the transport to the extent that some energy region can rather be considered as charge traps. Trap filling phenomena upon charge injection\textsuperscript{[25]} at the redox semiconducting polymer/electrolyte interface have been observed in electrochemical transistors.\textsuperscript{[26]} We believe that the self-discharge observed in those batteries is reminiscent of the electronic structure of the redox polymers, which can be seen as a Gaussian distribution in the energy scale rather than a specific well-defined energy level. During the charging process, the charge carriers are injected within the electronic levels of a Gaussian density of the redox polymers at a certain applied voltage. However, when left in an open-circuit condition, the injected charge carriers will relax to lower energy levels in the Gaussian distribution leading to a reduction of the open-circuit voltage with time (Figure 4b).

To confirm that the voltage decay in regime 2 is associated with the redox potential of polymer electrodes, two complementary cells, L–C/PAAK/AC and AC/PAAK/P–C, were prepared. In those two devices, the redox peaks of the redox polymers can be easily decoupled because the counter electrode is a capacitive AC electrode. As can be seen from Figure 4c, the regime 2 in self-discharge of device L–C/PAAK/AC starts at around \( \approx 0.9 \text{ V} \), which is associated with the reduction peak of L–C (Figure 4d). Similar observation was found for the case of P–C as the reduction peak of P–C is around 1.1 V and the corresponding voltage plateau starts at \( \approx 1.1 \text{ V} \). These results support our hypothesis that the plateau voltage in regime 2 is associated to the redox potentials of the polymer in the electrodes.

4. Conclusion

In conclusion, several reports have demonstrated that P–C/PAAK/L–C is an organic battery with various unique features that could potentially make it to the market. This all-organic battery is not only based on low-cost polymers, one being even a biopolymer, but also functions well with an aqueous electrolyte to ensure safety. Because of those promising attributes, and a good self-discharge behavior using the concept of “water-in-polymer salt electrolyte” (WIPSE), those studies motivate to understand more about the self-discharge mechanism in those lignin batteries.

We have ruled out that proton and oxygen reductions are involved in the self-discharge curve (regime 2). This suggests that the PAAK electrolyte is stable enough and that the self-discharge mechanism is related to an electronic phenomenon coupled to the relaxation of charges in the density of states of the redox polymers.

From an applied point of view, this study does not only confirm the unique slow self-discharge with highly concentrated PAAK-PAAH electrolytes, but it demonstrates that the manufacturing of those all-organic low-cost battery can be done in air, in atmospheric condition with little effect on the electrical performance. The best pH can be chosen to combine long-term stability (avoid corrosion) and high energy density. Hence, mass manufacturing techniques, such as roll-to-roll coating or printing techniques in air, are truly making sense for those scalable, robust, low-cost, and sustainable organic batteries.

Supporting Information

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

Acknowledgements

This work was primarily supported by the Proof-of-Concept project “Paper Batteries (KAW 2019.0344)” and “high-voltage aqueous electrolytes (KAW 2020.0174)” and the “Wood Wallenberg Science Center” funded by Knut and Alice Wallenberg (KAW) foundation. This work also includes some support from the Swedish Research Council (grant no. 2016-05990) and the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LIU No. 2009-00971). M.B. acknowledges the Wallenberg Scholar grants from KAW. The authors are grateful to Jakob Nilsson, Anders Hägerström, and Peter Ringstad for scientific discussions.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords

lignin, organic batteries, self-discharge, water-in-polymer salt electrolytes (WIPSEs), water-in-salt electrolytes

Received: May 12, 2022
Revised: July 3, 2022
Published online: July 19, 2022

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