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Hybrid biopolymer electrodes for lithium- and sodium-ion batteries in organic electrolytes

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The use of earth abundant and renewable materials is encouraging for the future development of environmentally clean, safe and affordable electrodes for lithium- and sodium-ion batteries. Biohybrid electrodes based on lignin and several conducting polymers have been studied mainly for supercapacitor applications. Here, we show that biohybrid electrodes containing natural lignin and PEDOT conjugated polymer serve as electroactive materials for lithium- and sodium-ion half cells using liquid organic electrolytes. Reversible discharge capacities of 74 mAh.g⁻¹, at C/20 (4 mA.g⁻¹) rate, were achieved in the voltage range between 1 V to 4.5 V, with peak values of up to 159 mAh.g⁻¹. These properties make natural lignin-PEDOT hybrid material a suitable organic positive electrode in Li- and Na-ion batteries.

Introduction

Electrochemical storage of energy in batteries is desirable because of their relatively high-energy density, flexibility and scalability.1-3 Lithium ion battery technology have occupied practically the whole niche of the market for power electronics and portable devices because of its high energy density compared to other technologies.5 Research on sodium ion batteries is advancing fast6 towards lowering the cost of the batteries so they can be applied for storing large amount of energy from renewable sources. The interest is extensive due to the following reasons:5-8 (i) the high abundance and ubiquitous distribution of sodium; (ii) similar energy density than lithium; (iii) copper current collector can be replaced by lighter aluminium diminishing the penalty in the gravimetric energy density on going from lithium to sodium; (iv) expected rising cost of lithium because of the increase on the long– term demand.

Numerous inorganic compounds, mainly oxides, phosphates, and alloys of Na with group IV and V elements have been assessed for Na⁺ ion storage.9-11 Although most of them have shown gravimetric capacity and long cycle life comparable to those evidenced by their lithium analogues, still some issues related to kinetics limitations during Na⁺ ion intercalation12 as well as cost remain unsettled. So, alternative chemistries and materials are needed, for both lithium and sodium battery technologies so they can achieve the required electrochemical performance at relatively low–cost while meeting the safety and environmental friendless requirements.13 Because large devices for storing huge amount of electricity are needed, the most important properties of the battery materials are not their energy density and efficiency, but more importantly a very prolonged life and the use of safe and abundant materials.14 Electrodes based on redox active polymers that might ultimately have been prepared from renewable biomass appears to be one attractive solution.15-17 As a flexible macromolecular framework, organic polymers can accommodate large cations reversibly without much spatial hindrance, therefore enhancing the kinetics for cation insertion and extraction reactions.18-21 Moreover, most of them do not contain costly and unfriendly metals and are profuse all over the earth.22 Quinone-based materials have been studied as organic positive-electrode materials, since the quinone moieties undergo a two-electron redox reaction which should lead to a high discharge capacity at relatively high voltages vs Li or Na plating.23,24 Natural lignin is the most abundant aromatic polymer on earth. In aqueous media, lignin can reversibly store two electrons and two protons by using the redox chemistry of the quinone groups located in its macromolecular structure.25,26 Interestingly, in non-aqueous solvents quinone can be reversibly reduced in two one-electron steps to the anion radical and dianion, respectively.27-29 Hybrid polymer electrodes containing quinone redox moities and conjugated units have recently show exceptional electrochemical proton storage properties in organic electrolyte.30 The strong ionic interaction between the reduced carbonyl functionality and small cations like Lithium

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Sustainable Energy Fuels, 2017, 00, 1-7 | 1
(Li⁺), Sodium (Na⁺), Magnesium (Mg²⁺) and Aluminium (Al³⁺) has been exploited to increase the gravimetric energy by largely modifying the voltage of reaction.²⁸ Primary lithium batteries based on hydrolysis lignin as positive electrode material composite containing carbon and a polymeric binder have been developed.³¹ More recently, PEDOT/lignin composites have also been studied as cathode material for sodium ion batteries with ionic Liquid electrolyte delivering a maximum capacity of 70 mAh.g⁻¹ at 25 mA.g⁻¹.³² Liquid electrolytes are much lower cost and should lead to more viable Na-ion batteries. Here, we study the possible storage mechanisms of natural lignin, PEDOT and Lignin/PEDOT hybrids in a series of organic liquid electrolytes for Lithium and Sodium ion batteries. Given the insulating character of lignin, the electrochemical performance is greatly enhanced when it is hybridized with a conjugated polymer (PEDOT) as biopolymer electrode material. To the best of our knowledge, this is the first report on the use of natural lignin as electrode material for Lithium and Sodium ion batteries with liquid organic electrolytes.

Experimental

Lignin Extraction.

Natural lignin was isolated from black liquor after treatment at room temperature by adding 125 ml of 1 M sulfuric acid (H₂SO₄) to 20 ml of black liquor. After precipitation, the raw lignin was collected by centrifugation (4000 rpm during 5 minutes). The solid was dissolved with sodium hydroxide (NaOH, 0.1 M) and precipitated again with 1 M H₂SO₄ in a volume ratio Lignin:NaOH/H₂SO₄ 1:2, this procedure was repeated five times. The purified biopolymer was separated by centrifugation and dried at 80 °C under vacuum overnight. Purification of lignin with NaOH was confirmed by analysing the polymer by EDX in the SEM. The results shown in Table S1, demonstrate that after purification, the percentages of sodium, polymer by EDX in the SEM. The results shown in Table S1, demonstrate that after purification, the percentages of sodium, oxygen and sulfur largely decrease on the sample.

Synthesis of Lignin/PEDOT polymers.

Lignin/PEDOT polymers were synthesized via chemical oxidative polymerization of EDOT monomer in the presence of lignin, by using iron (III) Chloride as catalyst and Sodium Persulfate as primary oxidant at room temperature during 8 hours, as explained elsewhere.³³ The initial Lignin:EDOT mass ratios used were 0:100, 20:80, 40:60 and 60:40 yielding the so called PEDOT, Lig/PEDOT 20/80, Lig/PEDOT 40/60 and Lig/PEDOT 60/40 polymers, respectively. In order to confirm the polymerization of EDOT in the presence of lignin and the composite character of the final products, Fourier Transform Infrared (FTIR) and Thermogravimetric (TG) analyses experiments were performed on the lignin, and the Lig/PEDOT polymers.

Characterization of Lignin and Lignin/PEDOT polymers.

The chemical composition of natural lignin before and after purification was analyzed by energy dispersive X-rays (EDX) in a Quanta 200 FEG (FEI) microscope. FTIR spectra were acquired at room temperature using a Thermo Scientific Model Nicolet 6700 FT-IR spectrometer, collecting 10 scans in transmission mode using KBr pellets. TG analyses were performed on a TGA Q500 (TA Instruments). Measurements were carried out by heating around 3 mg of sample at 10 °C min⁻¹ under nitrogen atmosphere from room temperature to 800 °C.

Electrochemical testing.

Electrochemical tests were conducted in 2032 coin cells, which were assembled in an argon filled dry box. The working electrodes were produced in powder form and tested in this way as cathodes against Lithium (Li) or Sodium (Na) foil. The cathodes were composed of 4-5 mg of lignin_C65 (80 wt% of lignin and 20 wt% of Timcal super C65 conductive carbon black), PEDOT or Lignin/PEDOT polymers. When carbon was included, the powder electrodes were prepared by mixing the active polymer with Timcal super C65 conductive carbon black by hand grinding in a mortar. The electrolytes used were lithium perchlorate (LiClO₄), lithium hexafluorophosphosphate (LiPF₆), sodium perchlorate (NaClO₄), and sodium hexafluorophosphosphate (NaPF₆) in a 50/50 vol % mixture of ethylene carbonate and dimethyl carbonate (EC/DMC). LiClO₄ and LiPF₆ were used with Li anode, while NaClO₄ and NaPF₆ with Na anode. Lignin, Lignin/PEDOT polymers and carbon C65 were dried under vacuum at 80 °C overnight prior to battery assembly, while the metal anodes and electrolytes were kept inside the dry box. The battery cycling rate is reported in terms of C/n, where n is the number of hours used to fully charge or discharge the battery based on the experimental capacity of lignin-polymer hybrid bioelectrodes of 80 mAh.g⁻¹, reported by Milczarek and Inganäs.²⁶ Then, our cells were cycled at C/20 (4 mA.g⁻¹), C/10 (8 mA.g⁻¹), C/2 (40 mA.g⁻¹) for five cycles each rate, and finally C/20 (4 mA.g⁻¹) for 25 cycles. The capacities were calculated per gram of Lignin/PEDOT in the electrode. All the experiments started with a reduction step as the PEDOT is already oxidized.

Results and discussion

Figure 1. Schematic structure of PEDOT (blue), lignin (olive), and Lig/PEDOT (a) and of the Lignin/PEDOT batteries assembled (b).
Lignin/PEDOT polymers were synthesized via oxidative polymerization of EDOT in presence of lignin as previously reported.\textsuperscript{33} Figure 1 shows the schematic structure of the Lignin/PEDOT hybrids. The thermal and chemical characterization of lignin, Lignin/PEDOT and PEDOT is shown in Figure S1. Lignin/PEDOT hybrid biopolymers showed infrared bands characteristic of both, lignin and PEDOT; as well as thermal properties intermediate in between these materials, confirming the successful hybridization between PEDOT and lignin. Upon battery assembly, the OCV of all Lig/PEDOT hybrids varied between 2.5 and 3.0 V vs Na\textsuperscript+/Na or Li\textsuperscript+/Li, suggesting the presence of oxidized species (either quinones or oxidized PEDOT or both). The first galvanostatic cycle for all the compounds is shown in Figure S2 and their respective coulombic efficiencies are listed in Table S2. Natural lignin stores cations most probably by ionic coupling with the reduced carbonyl functionalities from lignin, while the PEDOT storage depends on the ingress/egress of the ions.\textsuperscript{27,32,34} The extra capacity during charge of the lignin_C65 might come from the remnant sodium from the NaOH used during purification of the extracted biopolymer. The Lig/PEDOT hybrids showed capacities in the range of 5-35 mAh.g\textsuperscript{-1} during the first reduction, likely due to Li or Na ion intercalation along with quinone reduction. They all showed much larger capacities during the subsequent first oxidation, although this was quite dependent on the PEDOT content, but also on the electrolyte, which suggests that most of this capacity must be related to anion insertion into the PEDOT/Lignin. Although a contribution from electrolyte decomposition cannot be ruled out, in most cases the oxidation capacity was higher in the presence of LiPF\textsubscript{6} than LiClO\textsubscript{4}, the former being prone to oxidation at lower voltages, which suggests this was not the main source of irreversible capacity.

The reversible capacities during the second (Figures 2 and S3) and subsequent cycles increased for all the hybrid biopolymers in each of the different electrolytes. Figure 2a shows the galvanostatic voltage profile of lignin_C65 with lithium and sodium perchlorate and hexafluorophosphate. All the discharge curves showed a change in slope at around 3 V where the reduction of lignin along with cation (i.e. Li\textsuperscript{+} or Na\textsuperscript{+}) insertion started. The highest discharge capacity, 60 mAh.g\textsuperscript{-1}, was achieved in both, LiClO\textsubscript{4} and NaClO\textsubscript{4} based organic electrolytes. In the case of the hexafluorophosphate electrolytes, the capacities achieved were only 22 and 28 mAh.g\textsuperscript{-1}, for LiPF\textsubscript{6} and NaPF\textsubscript{6}, respectively. Despite the observed trend in the discharge capacity, mainly depending on the anion, the behaviour of the lignin_C65 electrode during charge varied mostly according to the cation. In LiClO\textsubscript{4} and LiPF\textsubscript{6}, the charging redox process started at 1 and 1.1 V, respectively. Then, several changes in slope were observed starting at 2.7 and 3.4 V, respectively. The total charge capacity for LiClO\textsubscript{4} and LiPF\textsubscript{6} were approximately 67 and 20 mAh.g\textsuperscript{-1}, respectively.

In NaClO\textsubscript{4} and NaPF\textsubscript{6}, several changes in slope were observed only above 2.3 V for both electrolytes. The total charge capacity was approximately 103 and 51 mAh.g\textsuperscript{-1}, respectively. Generally, quinone-based materials in organic electrolytes present a series of asymmetric plateaus around 2.5 – 3.5 V. The voltage of these plateaux depends on the chemical environment of the quinone moieties.\textsuperscript{24,35,36} The charge capacity was higher than that of discharge in LiClO\textsubscript{4}, NaClO\textsubscript{4} and NaPF\textsubscript{6} with extra capacities of 12, 72 and 82 % respectively being achieved during charge. In LiPF\textsubscript{6}, there was an irreversible capacity of about 2 mAh.g\textsuperscript{-1} or nearly 9 % of the discharge.

Figure 2b shows the galvanostatic discharge and charge of PEDOT in each of the different electrolytes during the second cycle. In contrast to lignin_C65, which showed a steeper profile down to 1V, the redox processes in PEDOT seemed to occur all at voltages above 2.5V vs A’/A, with negligible capacity below that voltage only in the case of NaPF\textsubscript{6} containing electrolyte. The redox mechanism of conducting polymers has been reported to comprise the intercalation of both electrolyte’s ions.\textsuperscript{37} The charging capacities were about 44 and 23 mAh.g\textsuperscript{-1} for LiClO\textsubscript{4} and NaClO\textsubscript{4}, respectively. In LiPF\textsubscript{6} the discharge and charge capacities were 50 and 120 mAh.g\textsuperscript{-1}, respectively. In NaPF\textsubscript{6} discharge and charge capacities were 34 and 53 mAh.g\textsuperscript{-1}, respectively. Figure 2c presents the electrochemical behaviour of Lig/PEDOT 20/80 during the second cycle. This biopolymer showed the
Lig/PEDOT 20/80 started at voltages below 3 V vs A/A' while they only started at 3.1 to 3.4 V vs A/A' in PEDOT. As a result, there was an increase in the capacity values, in comparison with bare PEDOT and lignin, suggesting a synergistic effect that might come from the coupling of their redox processes, i.e. the swelling of the PEDOT which facilitates ion transportation may help the electrochemical reaction of the lignin, which being so insulating also got favoured by the high content of conducting PEDOT.

The intercalation of the cations in Lig/PEDOT 20/80 depended on the anion present in the electrolyte. At around 2.4 V, Lig/PEDOT 20/80 stopped intercalating cations in LiClO$_4$, LiPF$_6$ and NaClO$_4$, while in NaPF$_6$ there was just a change of slope, after which the intercalation continued.

The discharge capacities for Lig/PEDOT 20/80 were 82, 79, 71 and 62 mAh.g$^{-1}$ in LiPF$_6$, NaPF$_6$, LiClO$_4$, and NaClO$_4$, respectively. During charge, the de-intercalation of the cations was independent of the electrolyte and started around 2.7 V.

In order to compare the evolution upon cycling a more detailed evaluation of the galvanostatic curves at C/20, with the capacities normalized to their maximum values, are shown in Figures 3 and 4. In general, the intercalation of ions in PEDOT and Lig/PEDOT 20/80 started at higher voltages than for lignin_C65 likely due to better conductivity and less resulting polarization; while the de-intercalation seemed to initiate first in lignin than in the other two polymers. As mentioned before, lignin’s galvanostatic curves did not show a clear plateau and Lig/PEDOT 20/80 curves resembled the ones observed for PEDOT.

PEDOT and Lig/PEDOT 20/80 achieved most of their discharge capacity at higher voltages than lignin_C65, this might be a consequence of much slower cation transfer through lignin. By using Lig/PEDOT biopolymers as cathodes, we took advantage of the ability of both initial materials to store energy; however, excess of lignin in the biopolymer might result in a decrease of the accessible electroactive sites.

Figure 4 shows the results of cycling lignin_C65, Lig/PEDOT 20/80 and PEDOT at different rates in each of the electrolytes. It can be seen that in LiClO$_4$ (Figure 4a), Lig/PEDOT 20:80 presented the most favourable combination of total capacity (62 mAh.g$^{-1}$ at C/20) and capacity retention (44 % after 25 cycles at C/20). Lignin_C65 showed a similar performance, yet the capacity values were lower and less stable while PEDOT behaved poorly. The other Lig/PEDOT proportions did not intercalate lithium ions (Figure 5a) in this electrolyte. This behaviour proves that in this electrolyte, lignin requires either a conductive filler (C65) or a high proportion (80 %) of electron conductor polymer.

In LiPF$_6$, Lig/PEDOT 20:80 exhibited the highest capacity of all the materials (Figure 4b) and showed an improvement in cycle-life in comparison to the same material in LiClO$_4$. Capacity values up to 92 mAh.g$^{-1}$ at C/20 and capacity retention of 70 % after 25 cycles at C/20 were achieved with this material. In contrast to the performance in LiClO$_4$, all the other Lig/PEDOT proportions (Figure 5b) inserted lithium ions in the cathode, showing an improvement over the intercalation properties of lignin.
Quite different results were achieved when cycling with Na electrolytes vs Na+/Na. In the case of NaClO4 (Figures 4c and 5c), the C65 conductive filler allowed the continuous insertion of ions in the lignin cathode, maintaining 48% of its initial capacity. The hybridization of Lignin and PEDOT worsened the Na+ intercalation abilities in NaClO4. Lig/PEDOT 20:80 achieved the highest capacity during the second discharge, but the capacity faded very fast.

A contrasting effect is observed in NaPF6 (Figure 4d and Figure 5d), where all the lignin-derived materials presented electrochemical activity even after 40 cycles. The increment on the PEDOT proportion enhanced the capacity values of the lignin, with a maximum value of 83 mAh.g⁻¹ at C/20, for Lig/PEDOT 20:80.

In general, the behaviour of these cathode biohybrid materials seemed to be highly dependent on the salt anion. Indeed, comparing the plots on the left and the right of Figure 4 and Figure 5, it is evident that the electrochemical process was enhanced in the Lig/PEDOT hybrids when PF6⁻ was the anion counter-balancing the alkali metal cation.

Incremental capacity analysis (ICA) is a powerful technique to obtain information on aging mechanisms. ICA is based on dQ/dV vs. V plots and transforms voltage plateaus and inflections points in voltage curves into dQ/dV peaks.38 To investigate the aging mechanism of Lig/PEDOT 20/80 in the different electrolytes, ICA of different stages of cycling, i.e. 2nd, 16th, and 40th are shown in Figure 5. Cycle 16th corresponds to the first cycle after cycling at different current densities.

In general, the charging and discharging peaks of Lig/PEDOT 20/80 were stochastic. This might be caused by resistivity of the electrodes and difficulty for Li⁺ and Na⁺ to intercalate.

During cycling, two common characteristics were observed in the dQ/dV plots in all the electrolytes. On the one hand, diminishing in the peaks intensity indicated loss of active material, meaning there was a loss of electrical contact coming from a percolation origin.39

On the other hand, the shifting towards higher/lower voltages during discharge/charge could suggest an evolution of the composition and morphology of the electrode material or an indication of underdischarge and undercharge. The fact that the underdischarge and undercharge effect appeared on both discharge and charge with a similar magnitude, indicated that this increase of polarization was ohmic in nature.38

In order to improve the electronic conductivity and cation diffusion, a composite made out of 20 wt% Timcal super C65 conductive carbon and 80 wt% Lig/PEDOT 20/80 (herein Lig/PEDOT 20/80 + C65) was tested as cathode for Li- and Na-ion batteries. LiPF6 and NaPF6 were selected as the electrolytes, given the excellent performance of Lig/PEDOT 20/80 in them. Figure 6 shows the cycle-life data of Lig/PEDOT 20/80 and Lig/PEDOT 20/80 + C65 in LiPF6 and NaPF6. The inclusion of C65 in the biopolymer electrode improved the discharge capacity values up to 119 mAh.g⁻¹ and 159 mAh.g⁻¹ at C/20 in LiPF6 and NaPF6, respectively. These values were calculated per gram of Lig/PEDOT.

The galvanostatic curves of the Lig/PEDOT 20/80 with and without C65 (Figure S6) showed the same general trend. Nevertheless, when C65 was added to the biopolymer and the composite tested in LiPF6 (Figure S6a), the peaks intensity in the dQ/dV plots was increased, showing that C65 improved the Li⁺ diffusion inside the Lig/PEDOT biopolymer.

Moreover, when the composite was tested in NaPF6 (Figure S6b), the insertion/de-insertion occurred at higher/lower voltages than when Lig/PEDOT 20/80 was tested and the intensity of certain peaks was enhanced. The combination of these two phenomena, resulted in the increase of the capacity values when C65 was added to the biopolymer.

The difference in the rate capabilities of the biopolymers in LiPF6 and NaPF6 might be caused by the reduction potential difference between the two anodes. For example, in the case of NaPF6, the highest oxidation peak observed during the second cycle was at 4.25 V vs. Na/Na⁺; while in LiPF6 the peak is just partially undertaken (onset at 3.9 V vs. Li/Li⁺). This might cause an initial enhanced capacity for NaPF6, but also a lessened capacity retention. However, the complete mechanism should be further investigated in future studies.
The performance of these biopolymer Lig/PEDOT hybrid electrodes is competitive with other electrode materials and outperforms other lignin based bulk electrode materials. Hydrolysis lignin has been studied as cathode for Li-ion primary batteries at low-rate. The hydrolysis lignin cathode was composed of 76 % active component and the final electrode was heated at 280 °C for 2 hours and tested in 1 M LiBF_4 in y-butyrolacton and 1 M LiClO_4 in propylene carbonate, delivering up to 185 mAh.g\(^{-1}\) at 75 μA.cm\(^{-2}\). Lignin/PEDOT hybrids have been recently studied for sodium battery applications in BMPyrTFSI:NaTFSI (20 mol%) and EMImFSI:NaFSI (20 mol%) electrolytes achieving at 25 mA.g\(^{-1}\) up to 46 and 70 mAh.g\(^{-1}\), respectively. By testing our electrodes derived from black liquor, rather than commercial lignin we are actually using a low cost by-product from paper industry. Moreover, by employing more conventional electrolytes with smaller anions, the ion exchange was improved and therefore the capacity values were enhanced. Furthermore, in the present work the percentage of active material within the electrode was increased from 65 to 80%; therefore, enhancing the gravimetric energy density. Further capacity improvement could be expected from electrode optimization in the form of thin films.

Conclusions

To sum up, in this work we synthesized and investigated lignin, PEDOT and Lignin/PEDOT biopolymers as bulk electrode materials for electrochemical energy storage in lithium and sodium ion batteries. The interesting synergistic behaviour of Lignin/PEDOT biopolymer hybrids lead to high storage capacity, i.e. ~50 mAh.g\(^{-1}\) at C/20 in LiPF_6 and NaPF_6. To enhance to the maximum the delivered capacity, a composite made out of C65 and a Lignin/PEDOT biopolymer was tested as cathode against Lithium and Sodium, peak values up to 159 mAh.g\(^{-1}\) and stable values of 74 mAh.g\(^{-1}\) were attained. This work demonstrates that biopolymers based on lignin, a renewable and inexpensive material, can be used as sustainable electrodes with highly efficient electrochemical energy storage for Lithium- and Sodium-ion batteries. Surface and interface engineering is essential to improve the electrochemical performance of Lignin/PEDOT materials for Lithium- and Sodium-ion batteries.

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6 | Sustainable Energy Fuels, 2017, 00, 1-7

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Hybrid biopolymers, composed of Lignin and PEDOT, show enhanced storage capacity for Lithium- and Sodium-ion batteries.