Polydopamine-based redox-active separators for lithium-ion batteries

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1. Introduction

The ever-increasing demand for efficient energy storage in portable devices, electrical vehicles and large-scale energy storage systems has pushed the development of lithium-ion batteries (LIBs) towards the development of devices with higher energy and power densities [1–3]. These efforts have so far mainly involved improvements of the electrode materials via the development of new or functionalized separators, although it is well-known that the properties of the separators can affect the battery performance significantly, mainly due to its influence on the ionic transport pathways and the current density distributions at the electrodes [7,8].

While contemporary LIB separators are dominantly based on polyolefin (polypropylene: PP or polyethylene: PE) materials, their intrinsic drawbacks, e.g. poor wettabilities with respect to conventional electrolytes and insufficient thermal stabilities at elevated temperatures [9–12], have led to attempts to develop improved polyolefin separators [13–15] as well as new alternative separator materials [16–21]. To enable a utilization of new generations of materials and the realization of energy storage devices with high energy and power densities, functionalized separators have recently attracted significant attention. Conductive coatings [22,23], ion adsorbing agents [8,24], size excluding layers [25,26], permselective media [27,28], as well as different combinations of the latter approaches [29], have hence been used in conjunction with commercial separators, or separators based on new materials, to alleviate unwanted diffusion of specific ions (e.g. polysulfide ions and Mn2+) [30]. Separators composed of several layers have likewise been developed to tackle safety issues associated with lithium dendrite formation on lithium metal electrodes via the use of functionalized intermediate layers enabling early detection [31] or scavenging of dendritic lithium [32]. However, as the majority of the aforementioned functionalization approaches resulted in thick
or densely structured separators that increased the volume of the battery and/or gave rise to increased cell resistances, the use of these separators had an adverse effect on the energy and power densities of the batteries. Furthermore, since the latter functionalized separators were generally designed for specific electrode materials and batteries, general approaches to simultaneously increase the energy and power densities of LIBs by merely functionalizing the separator still remain scarce.

One possibility would, however, be to use redox active separators, such as the recently described nanocellulose and polypyrrole (PPy) bi-layered separator [33], which can be used with common cathode materials (i.e. at potentials >2.5 V vs. Li+/Li). The latter separator was composed of a 3 μm thick nanocellulose layer, functioning as the true separator layer, and a 7 μm thick porous PPy/nanocellulose composite layer functioning both as a mechanical support and a redox-active layer providing additional capacity to the cell. As the total thickness of the redox-active separator can be made equal to that of the conventional separator, the redox active separator can increase the volumetric capacity of the cell significantly. Since the aforementioned PPy based redox-active separator was designed to operate as an extra cathode material, there is also the corresponding possibility to develop a redox-active separator that functions as an additional anode material. This is, unfortunately, complicated by the fact that there are only a rather limited number of polymers with redox potentials in the appropriate potential region. A redox-active separator that can contribute extra capacity in a potential region of common anode materials is hence still to be demonstrated.

During the last decade there has been a growing interest in the use of renewable and naturally abundant materials in energy storage devices, such as batteries and supercapacitors [34–37]. This has generated a large interest in the use of cellulose and its derivatives, in e.g. binders [38], gel polymer electrolyte components [39] and flexible substrates [40,41]. Cellulose is presently also considered a promising alternative materials for LIB separators [42–44], due to its excellent hydrophilicity and thermal stability [10,18,20]. Another interesting renewable material is dopamine, which is a major pigment in natural melanin and which has found to play an essential role in the adhesion of mussels to solid surfaces [45]. Dopamine has abundant functional groups and can undergo oxidative self-polymerization in alkaline aqueous solutions to generate polydopamine (PDA) with different morphologies (e.g. thin film, spheres) depending on the choice of temperature, oxidant and reaction time [45]. Due to the excellent adhesion ability of PDA to virtually all types of organic and inorganic surfaces, PDA was first presented as a versatile surface coating material in 2007 [46]. More recently, PDA has been used in conjunction with energy storage devices as a carbon source [47] and as a hydrophilic coating on PE separators [12,13]. Due to its redox-activity, stemming mainly from the catehol groups [48], PDA has also been studied both as anode and cathode material [36,49] for LIBs and sodium-ion batteries. The PDA molecular structure is, unfortunately, complex and still not fully understood due to the complicated polymerization reaction yielding a multitude of different molecules [48]. PDA has, nevertheless, been found to exhibit interesting electrochemical behavior [36,49]. Its significant electrochemical activity within the potential region of interest in conjunction with anode materials and excellent adhesion to most surfaces make PDA a promising candidate for use in a redox-active cellulose based separator compatible with LIB anodes.

Herein, a new bilayer-structured redox-active separator, comprising a thin NCF layer and a thicker NCF/PPy/CNT composite layer, is manufactured and used to increase the capacity of the LIB anode. The polypyrrole based redox-active (PRA) separator consists of a 2 μm thick NCF separator layer and an 18 μm thick redox-active layer containing the PDA particles, CNTs and NCFs, where both layers are hydrophilic and thermally stable. The 2 μm thick electrically insulating NCS layer, which thus serves as the true separator layer, merely represents 8% of the volume occupied by a conventional 25 μm thick polyolefin separator. Meanwhile, the 18 μm thick highly porous redox-active layer acts both as a supporting layer, providing the required mechanical strength and flexibility, as well as a source of additional capacity in a potential window compatible with common LIB anode materials (i.e. 0–3 V vs. Li+/Li).

The performances of cells containing LTO and lithium metal (Li) electrodes in addition to either a PRA or a conventional PE separator demonstrate that the PRA cell exhibited higher capacities than the corresponding PE cell at all studied cycling rates. This can be explained by the higher ionic conductivity of the PRA separator and the redox-active properties of the PDA containing layer acting as an extension of the LTO anode. The main components of the PRA separator are biosourced and biodegradable, as the NCFs originally were extracted directly from sea algae by our group [50,51], while dopamine is a naturally occurring biomolecule employed in many different fields [46,52–54]. As the production of the PRA separator only involves self-polymerization of dopamine, sonication of NCFs and CNTs, as well as low vacuum filtration, the PRA separator is more environmentally friendly than the conventional fossil fuel derived polyolefin separators, particularly as the low-energy-demanding process readily can be scaled up. The present PRA separator approach therefore constitutes a new promising route towards the realization of more sustainable LIBs with increased energy and power densities.

2. Results and discussion

Composition, morphology and conductivity. As indicated in Fig. 1, the PRA separator or has a bi-layered structure with a pure NCF layer and a redox-active PDA/NCF composite layer. Scanning electron microscopy (SEM) images of the PRA separator, as schematically indicated in Fig. 2, confirmed the successful realization of the bi-layered structure as two distinct layers can be observed in Fig. 3a with the thin NCF layer and the porous redox-active PDA/NCF layer above and below the red dashed line, respectively. X-ray photoelectron spectroscopy (XPS) results (see Fig. 3e) clearly indicated the presence of N-containing species in the redox-active layer, which can be attributed to the presence of the PDA components. The presence of the PDA components was also verified in an Energy

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Dispersive X-ray spectroscopy (EDX) element mapping analysis of the redox-active layer (see Fig. S1), demonstrating that the nitrogen (as well as the carbon and oxygen) was distributed homogenously within the studied region.

As discussed in the literature [48], the PDA generating self-polymerization process is complicated by multi-step reactions and still not fully understood. It has, however, been proposed [48] that the PDA molecules mainly consist of covalently linked 5,6-dihydroxyindole (DHI) and 5,6-indolequinone (IQ) units (see Fig. 2), since a fraction of the DHI molecules can be oxidized to IQ molecules during the process [36,49]. Characteristic signals from the C=O groups in the IQ units were indeed observed in the XPS C 1s and O 1s spectra, as well as in the Fourier transform infrared spectroscopy (FTIR) spectra for the redox-active layer (see Fig. S2).

SEM images of the PRA separator also show that the thin but relatively compact NCF layer had the previously reported structure (see Fig. 3b) [20,33,55], whereas the redox-active layer featured a more porous structure with intertwined NCFs and CNTs forming a 3D network in which spherical PDA particles were present as fillers. SEM images of a NCF separator, a CNT/NCF sample and a PE separator are shown in Fig. S3. In the PRA design, the thin NCFs layer thus acts as the insulating layer that physically prevents direct contact of the anode and cathode in the battery, whereas the more porous redox-active layer provides the necessary mechanical support to the thin NCFs layer and also contributes to the energy storage capacity.

To demonstrate the mechanical functionality of the redox-active layer, a 3 µm thick NCF film (see Fig. S4) was also produced with the same paper-making method. This thin and unsupported NCF film was, however, difficult to peel off the filter membrane due to its strong interaction with the latter and its insufficient mechanical strength. Even though a 5 µm thick NCFs film could be produced, the handling of such a thin NCF film was rather difficult due to electrostatic forces and its low mechanical strength. These findings, which clearly show the problems associated with the use of NCF-based separators with a thickness of up to 5 µm, indicate that it is practically difficult to increase the volumetric capacity of the batteries by employing such a thin separator. This problem is circumvented using the PRA approach as the redox-active PDA containing layer also serves as a mechanical support for the NCF separator layer that can then be made as thin as 2 µm. This consequently means that the electro-inactive volume of the PRA separator can be reduced to only that of the 2 µm thick NCFs layer. If the capacity of redox-active layer can indeed be employed, the energy density can consequently be increased compared to that for a conventional cell comprising a ~25 µm thick conventional separator.

It is worth noting that the porous redox-active layer not only should provide efficient electron transfer pathways due to the included CNTs but also should facilitate the Li⁺ mass transport required by the PDA electrochemical reactions. Since the PDA containing redox-active layer practically serves as an additional anode material present it could be argued that the same effect could be obtained by using a thinner conventional separator and a thicker layer of the anode material. As already indicated, the use of 5 µm thin separators is, however, not straightforward. Moreover, the use of a thicker anode material would not necessarily result in the expected increase in the capacity of the anode due to the increased diffusion length in the anode material. As the diffusion time is proportional to the square of the diffusion length (e.g. the thickness of the anode material), an increase of the electrode thickness by a factor of e.g. two would thus lead to a four-fold long diffusion time (e.g. cycling time) in order to access the total capacity. However, as the PRA separator is porous, the mass transport within the PDA containing layer is not an issue, which means that its inherent capacity should be readily accessed even at high cycling rates. Note also that the electrochemical reactions involving the conventional anode material should remain unaffected by the PDA containing layer, at least not in an electrolyte containing e.g. 1 M LiPF₆, due to the large excess of lithium ions.
The highly porous redox-active layer of the PRA separator should likewise be beneficial to decrease the cell resistance. The pore structure of a 20 μm thick PRA separator, which is described in Fig. 4, featured well-distributed large pores with an average size of 35 nm while the corresponding value for a 20 μm thick NCF membrane was 13 nm. More importantly, when compared with a conventional PE separator, Solupor®® the PRA separator exhibited a significantly higher specific pore volume in the studied region (see Fig. 4a, the areas under the curves), a higher porosity (32% vs. 20%) as well as a higher ionic conductivity (1.06 vs. 0.17 mS cm⁻¹, determined using ac impedance experiments after soaking with LP40 electrolyte), as can be seen in Table S1. The larger porosity, yielding a higher ionic conductivity and a lower cell resistance for the same separator thickness, should clearly be of significant importance to the rate performance of the LIBs. It can hence be concluded the LIB performance is expected to be enhanced with respect to the energy and power densities when replacing a conventional polyolefin separator with the proposed PRA separator. This conclusion is also supported by the electrochemical results described below.

**Thermal stability and electrolyte wettability.** Although the poor thermal stabilities and wettabilities of commercial polyolefin separators generally are tolerated in contemporary LIBs, much effort has been made to address these issues with polyolefin separators, as well as to search for better alternative materials [7,13]. The thermal stability is naturally very important to the battery safety at elevated temperatures, which makes this a particularly important question for batteries designed for high power.
applications. The wettability, which is coupled to the easiness of electrolyte incorporation into the pores of the separator, is of significant practical importance in the battery manufacturing process and naturally also depends on the choice of electrolyte [10]. Fig. 5 shows the results of thermal stability and wettability tests carried out with the PRA and PE separators. In the thermal stability test, in which the temperature was increased from room temperature to 150 °C, it was found that the size of the PE separator decreased significantly during the test while the PRA separator maintained dimensionally intact (Video S1). In the wettability test, where LP40 electrolyte was added drop by drop with a syringe onto the separators, it was found that the drops were absorbed more quickly by the PRA separator. This indicates that the PRA separator had a higher affinity for the LP40 electrolyte than the PE separator, as can be more clearly seen in the videos recorded during the experiment (Video S2). The good thermal stability and high wettability hence make the PRA separator a promising alternative to the commercial polyolefin LIB separators.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.jmat.2018.12.007.

**Electrochemical performance.** As mentioned above, the redox-active PDA containing layer should contribute to the charge storage capacity within a potential region compatible with those of typical LIB anode materials. To validate the PRA separator design and to evaluate the charge storage capacity of the PDA based redox-active layer, electrochemical measurements (i.e. cyclic voltammetric (CV) and galvanostatic (GS) experiments) were carried out with the PRA separator as one of the electrodes. In these experiments the CNT to PDA mass ratio in the redox-active layer was ~2:5. The employed two-electrode cells comprised a Li electrode and an electrolyte soaked PRA separator with the NCF layer in direct contact with the Li electrode. This cell configuration is referred to as the Li/PRA cell below.

Fig. 6a shows cyclic voltammograms depicting the first three cycles for the Li/PRA cell, recorded in a potential window between 0.1 and 3 V vs. Li⁺/Li at a scan rate of 0.1 mV s⁻¹. In agreement with the results of Sun et al. [36], a large irreversible discharge capacity was seen on the first cycle (see the reduction peak at about 0.7 vs. Li⁺/Li) while relatively stable cycling was observed on the subsequent cycles. The initial irreversible capacity can be attributed to a reduction of surface groups and the formation of a solid electrolyte interphase (SEI) layer on the CNTs [38]. This is further supported by the large irreversible reduction capacity seen during the first five cycles for a CNT/NCF sample in Fig. S6. On the first anodic scan, two small and broad bumps can, nevertheless, be seen at about 1.7 and 2.5 V vs. Li⁺/Li, most likely due to surface confined oxidation.

![Pore size distributions for the PRA, NCF and PE separators as well as Nyquist plots for symmetric cells (Cu/separator/Cu) cells equipped with PRA and PE separators, respectively.](image)

**Fig. 4.** Pore size distributions for the PRA, NCF and PE separators as well as Nyquist plots for symmetric cells (Cu/separator/Cu) cells equipped with PRA and PE separators, respectively. The high frequency intercepts in the Nyquist plots (see the insets) were used to calculate the ionic conductivities. The semicircle seen for the PRA separator stemmed from the PDA and CNT containing redox-active layer.

![Digital images taken before and after the thermal stability (left) and wettability tests (right) for the PRA (black) and PE (white) separators. The wettability tests can also be further studied in the videos found in the supporting information (i.e. Video S1 and S2).](image)

**Fig. 5.** Digital images taken before and after the thermal stability (left) and wettability tests (right) for the PRA (black) and PE (white) separators. The wettability tests can also be further studied in the videos found in the supporting information (i.e. Video S1 and S2).
reactions. The increasing cathodic current at potentials below about 0.5 V vs. Li⁺/Li can most likely be ascribed to the lithiation of the CNTs. The absence of a corresponding Li oxidation peak suggests that the corresponding delithiation step was incomplete, in good agreement with previous results for other carbon based electrodes [56–58]. As this phenomenon, which often is referred to as lithium trapping, was also seen on the second and third cycles, it appears as if the surfaces of the CNTs were partially re-oxidized on the anodic scan [56–58]. A small oxidation peak can also be seen at about 0.25 V vs. Li⁺/Li predominately on the second and third scans. The shapes of the second and third voltammetric cycles indicate that the PRA separator generally exhibited a capacitive behavior analogous to that seen for many carbonaceous materials.

Based on the second voltammetric cycle, the integrated discharge (i.e. cathodic) and charge (i.e. anodic) capacities of the PRA separator were approximately 375 and 309 mAh g⁻¹PDA (based on the PDA mass), excluding the capacity contribution from the CNTs (which includes double layer charging as well as faradaic reactions). The corresponding capacities, including the CNT capacity contributions were 452 and 375 mAh g⁻¹PDA. This consequently indicates that the capacity contribution from the PDA was about 80% both during charge and discharge in these voltammetric experiments.

The results of the galvanostatic cycling tests (see Fig. 6b) were generally consistent with the voltammetric results, as the first discharge of the PRA separator was associated with a large irreversible capacity. However, it was noted that the overall capacity (due to both the PDA and CNTs) calculated from the galvanostatic results (~200 mAh g⁻¹PDA) was much lower here than that in the voltammetric experiments (~452 mAh g⁻¹PDA). This effect was, most likely, due to the different experimental time domains as the time for a full voltammetric scan was ~16 h, whereas the corresponding time in the galvanostatic case was only ~2.3 h (see Fig. 6b inset). This would imply that the extent of the redox reactions of the redox-active layer were time-dependent.

When comparing Fig. 6b and S6, it can also be seen that the specific capacities of the PRA separator and the CNT/NCF layer were approximately the same (i.e. about 150 mAh g⁻¹ for a current density of 180 mA g⁻¹PDA) in the galvanostatic experiments. This together with the fact that the CNT to PDA mass ratio in the redox-active layer was ~2.5 indicates that about 60% of the capacity of the PRA separator stemmed from the PDA. It is hence clear that the capacity contribution from the PDA was smaller in the galvanostatic than in the voltammetric experiments, suggesting that the capacity due to the CNTs was more sensitive to the experimental time domain than the capacity due to the CNTs. The latter is not unexpected as the capacity of the CNTs stems from a combination of double layer charging and surface confined redox reactions, which both should

Fig. 6. Electrochemical performance of the PRA separator in the potential window between 0.1 and 3 V vs. Li⁺/Li. (a) Cyclic voltammograms showing the first three cycles for the employed Li/PRA cell using a scan rate of 0.1 mV s⁻¹. (b) The specific charge/discharge capacities of the Li/PRA cell as a function of the cycle number during 280 cycles obtained with a current density was 180 mA g⁻¹PDA. The voltage versus time profiles in the inset show the discharge and charge curves for the 50th cycle. (c) Voltage versus specific capacity curves for the Li/PRA cell depicting the 1st, 10th, 50th, 100th and 200th cycles. (d) Specific charge and discharge capacities of the Li/PRA cell as a function of the cycle number and current density (i.e. 90, 180, 360, 720 mA g⁻¹PDA).
be compatible with the use of high scan rates. Since the PDA was present as particles with a size of about 100 nm, the observed inability to access the same capacity at increased cycling rates is somewhat puzzling. It, however, appears as if a passivating layer is formed on the PDA particles, predominantly during the charging steps (i.e., during the oxidation of the PDA). Interestingly, the galvanostatic results also indicated the presence of an initial capacity increase for the Lj/PRA cell, which could be explained by an activation of the PDA spheres via an increase of their accessible surface area. The fact that this increase was predominantly seen for the charge capacity could be explained by the additional presence of the irreversible reactions taking place during the initial discharge steps.

As seen in Fig. 6b and c, there was a gradual decrease in the PRA capacity during prolonged cycling which most likely stemmed from a degradation of the electrochemical performance of the PDA. Nevertheless, the results still demonstrate that the PRA separator exhibited a capacity of about 180 mA h g⁻¹_PDA in the potential window between 0.1 and 3 V vs. Li⁺/Li at a cycling current density of 180 mA g⁻¹_PDA. This specific capacity, which incidentally is approximately half of that of graphene [59,60], shows that PDA is well-suited for use in this type of redox-active separators. Moreover, the high redox activity enables a higher volume capacity at lower current rates (-250 mA h g⁻¹_PDA at 90 mA g⁻¹_PDA), and maintained a capacity of ~100 mA h g⁻¹_PDA at a current density of 720 mA g⁻¹_PDA (see Fig. 6d). It can hence be concluded that the PRA separator can give rise to a significant capacity addition in the voltage region of interest when using common LIB anode materials. This is further demonstrated in the next section.

**Electrochemical performance of a proof-of-concept cell.** The basic idea when using the PRA separator is thus that the redox-active layer acts as both a part of the separator and as an extension of the anode. In this way it is possible to minimize the electroinactive volume within the cell and to increase its volumetric (and gravimetric) energy and power densities. To validate the concept the electrochemical performances of LTO/Li cells containing either a PE or a PRA separator were compared as is shown in Fig. 7. It should be noted that in the LTO/PRA/Li cell the redox-active layer was in direct contact with the LTO electrode. In Fig. 7a it can be seen that the PRA cell constantly exhibited higher capacities than the PE cell (i.e. 170 vs. 150 mA h g⁻¹ based on the LTO mass) at a cycling rate of 1 C. Comparisons of capacities based on the LTO weight were used for simplicity as both cells were equipped with identical LTO (and Li) electrodes. In analogy with the Li/PRA results discussed above, a large irreversible capacity was seen for the PRA cell but in this case the charge and discharge capacities increased rather than decreased somewhat during the cycling. The presence of initial irreversible reactions is also reflected in the Coulombic efficiency (CE) values for the PRA cell which increased during the cycling and stabilized at the same level as for the PE cell after about 20 cycles.

When scrutinizing the voltage versus specific capacity curves in Fig. 7b, it can further be seen that the PRA cell exhibited a larger capacity than the PE cell in the 1.5–3 V potential window. The latter can clearly be attributed to the presence of the PDA and CNT containing redox-active layer, and higher capacities were also seen for the PRA cell when increasing the cycling rate (see Fig. 7c). The largest difference between the PRA and PE cells was, however, seen at the lowest cycling rate in good agreement with the decreasing PDA capacity at increasing cycling rates discussed above. It is also clear that the PRA cell exhibited lower overpotentials both during charge and discharge which resulted in more well-defined plateaus than for the PE cell. These differences between the shapes of the voltage versus specific capacity curves, which became even more pronounced at higher cycling rates (see Fig. 7 d and e), can be ascribed to the lower electrolyte resistance of the PRA separator (see the high frequency intercepts in Fig. 6f). Moreover, the PRA cell exhibited a capacity of ~210 mA h g⁻¹_LTO at 0.5 C (vs. ~150 mA h g⁻¹_LTO for the PE cell) and ~110 mA h g⁻¹_LTO at 5 C (vs. ~70 mA h g⁻¹_LTO for the PE cell), confirming the enhanced rate capability of the cell with PRA separator seen in Fig. 7c. It should be noted that the theoretical capacity of LTO is 170 mA h g⁻¹_LTO and that the higher values presented above (e.g. 210 mA h g⁻¹_LTO) hence must be ascribed to the capacity contribution from the redox-active layer in the PRA separator.

The capacity contributions to the PRA separator from the PDA and CNFs were also evaluated at different cycling rates. In the employed potential window (i.e. 1–3 V, see Fig. S8), the CNFs featured a significantly lower capacity than in the 0.1–3 V region (i.e. ~30 versus ~185 mA h g⁻¹_CNT at 90 mA g⁻¹_PDA). The additional capacity due to the PRA separator in the LTO/PRA/Li proof-of-concept cell must consequently mainly be ascribed to the PDA since PDA was the major redox-active component in the redox-active layer (since m_PDA:m_CNT = 5:2) and the CNFs only had a capacity of ~30 mA h g⁻¹_CNT at 90 mA g⁻¹_PDA. In fact, the lower CNT capacity in the voltage range of 1–3 V is not surprising, given the significant capacity contribution seen at voltages below about 0.5 V in Fig. 6a and c. Regarding the capacity contribution from the PRA separator, it is important to mention that the magnitude of the absolute capacity increase depends strongly on the amounts of the anode material and the PDA as well as the employed voltage window. This means that the effects on the energy and power densities of different LIBs upon the replacement of the conventional separator with a PRA separator need to be determined for each individual LIB. The present results, nevertheless, clearly demonstrate the feasibility of the present redox-active separator concept, its potential usefulness when it comes to decreasing the electroinactive volume within the LIBs, and the possibility to enhance the energy and power densities of LIBs by merely exchanging the separator.

3. Conclusions

The development of future high-performance LIBs will most likely depend significantly on the development of new advanced separators since the use of functionalized separators constitutes a straightforward way of improving the battery performance. In the present work, a bi-layered polydopamine based redox-active separator (PRA), compatible with the potential region of typical anode materials, was designed and manufactured using biosourced and sustainable materials (i.e. nanocellulose and polydopamine) and a facile water-based paper-making process. By minimizing the thickness of the nanocellulose-based insulting layer to 2 μm and adding an 18 μm thick polydopamine and carbon nanotube containing redox-active layer as mechanical support, a new functionalized separator could be manufactured. Due to the thin insulting layer and the additional capacity provided by the redox-active layer, the capacity of a LiB could be increased merely by replacing the conventional separator without affecting the thickness of the cell or the electrode reactions at the anode and cathode.

The highly porous redox-active layer, which is electroactive between 0.1 and 3 V vs. Li⁺/Li, thus serves as an extension of the anode and can therefore be used irrespective of the choice of the anode material. While morphological and compositional evaluations demonstrated a successful manufacture of the PRA separator, further assessments also confirmed advantages of the PRA separator with respect to a commercial PE based separator regarding the thermal stability, wettability and ionic conductivity. Results obtained with a proof-of-concept LTO/Li cell further showed that the use of the PRA separator resulted in an enhanced energy storage capacity and rate capability compared to the corresponding cell.
containing a conventional PE separator. By making the major part of the LIB separator redox-active, the PRA approach not only provides a promising means for the simultaneous attainment of enhanced energy and power densities of LIBs, it also paves ways for the design of functionalized separators containing other interesting materials.

4. Experimental section

4.1. Materials

Cladophora cellulose powder (Batch NO. G3095-10), produced by the Cladophora green algae, was supplied by FMC Biopolymer USA. Dopamine hydrochloride, ammonia aqueous solution, multi-walled carbon nanotubes, lithium titanium oxide, Ketjen black, 1.0 M lithium hexafluorophosphate (LiPF6) in ethylene carbonate (EC)/diethyl carbonate (DEC) (1/1, v/v, BASF, i.e. LP40), Li foil (125 μm, Cyprus Foote Minerals) Solupor® (E/C08P01E, DSM), nylon filter membrane (Φ90 mm, 0.45 μm, Magna) were purchased from their indicated sources and used as received. The other materials (e.g. deionized water, ethanol, aluminum foil, copper foil) were all bought from commercial manufacturers and used without any further purification.

4.2. Preparation of PDA/NCF dispersion

In the preparation of the PDA/NCF dispersion, 200 mg Cladophora cellulose powder was ultra-sonicated with 70 mL deionized water in a sonication beaker for 15 min (VibraCell 750 W, Sonics, USA). The homogenous NCFs dispersion was then transferred to a flask where 40 mL ethanol, 20 mL deionized water and 2 mL ammonia aqueous solution had been pre-mixed for 20 min. The dispersion in the flask was stirred to allow homogenization for another 30 min prior to the drop by drop addition of a dopamine hydrochloride (DH) solution, prepared by dissolving 500 mg DH in 10 mL deionized water. The color of the mixture was immediately changed to salmon and then gradually to dark brown. The reaction was allowed to proceed for 24 h before using the PDA/NCF dispersion in the preparation of the redox-active layer. Another sample without any NCFs (but with the same amounts of solvents and other reagents) was also prepared for comparison. The latter was done to illustrate that when the NCFs were used in the synthesis, PDA spheres with smaller sizes could be obtained (see Fig. S5). A control sample with 10 mg CNTs and 50 mg NCFs was likewise produced with similar method (denoted as CNT/CNF).

Preparation of the PRA separator. The production of the PRA separator is schematically illustrated in Fig. 2. A 2 mg mL⁻¹ NCFs dispersion in deionized water was prepared by ultra-sonication. 4 mL of this dispersion was then diluted to 40 mL with deionized water. The PDA/CNT/NCF dispersion was then prepared by mixing 10 mL of the aforementioned PDA/NCF dispersion, 8 mg CNTs, 4 mg NCFs in 20 mL ethanol and 30 mL deionized water, followed by ultra-sonication for 15 min. The PRA separator was then manufactured by filtering the PDA/CNTs/NCFs dispersion on top of a filtered NCFs layer at a reduced pressure. The obtained wet PRA membrane was dried at room temperature overnight in a Petri dish, followed by heat treatment at 150 °C for 12 h. The PRA membrane was subsequently cut into ø20 mm discs and dried in a vacuum furnace at 120 °C overnight before further use. The PDA mass fraction in the PRA separator was determined by weighing the latter, based on the known masses of the other components.

Characterization of the PRA separator. The morphology of the samples was studied with a field emission scanning electron microscope (Zeiss Leo1550, Germany) and the element mapping of the redox-active layer was obtained using EDX. The XPS spectra were obtained with a Physical Electronics Quantum 2000 Scanning ESCA spectrometer equipped with monochromatized Al Kα.
radiation ($\text{hv} = 1486.7 \text{ eV}$). FTIR characterizations were performed with a Bruker FTIR66v/s spectrometer using an attenuated total reflectance sample holder at a resolution of 4 cm$^{-1}$. The nitrogen sorption analyses were performed at $-194^\circ\text{C}$ to examine the mesopores (i.e. pores with a diameter of 2–50 nm [61]) of the separators with a surface area analyzer (Micromeritics ASAP2020). The pore size distributions were determined with the Barrett-Joyner-Halenda (BJH) method based on the desorption processes. The porosities of the separators were calculated based on their apparent and bulk densities.

4.3. Electrode and cell preparation

LTO electrodes were prepared by first mixing LTO, carbon black and polyvinylidene fluoride powders in a weight ratio of 80:10:10 with N-Methyl-2-pyrrolidone as the solvent in a ball-milling jar. The slurry was then intensely mixed by planetary ball-milling for 1.5 h and coated onto an aluminum foil. The electrode foil was then allowed to dry at 100 $^\circ\text{C}$ in the coating machine for 15 min before it was cut into $\varnothing 13$ mm electrode discs and transferred into an argon-filled glove box. Lithium metal was cut into $\varnothing 14$ mm circular discs which were then used as combined counter and reference electrodes. The bare copper and aluminum electrodes ($\varnothing 13$ mm discs) were prepared and cleaned with ethanol before transfer into the glove box. Two-electrode pouch cells were assembled by sandwiching the electrolyte-soaked separator between the LTO electrode and the Li foil prior to sealing with a sealing machine in the argon-filled glove box (water content <1 ppm, oxygen content <1 ppm).

Electrochemical analyses. Electrochemical impedance spectroscopy (EIS) measurements in the frequency range between 10$^{-1}$ and 10$^2$ Hz were conducted to measure the impedance of symmetric (copper/separator/copper) cells at the open circuit voltage using a VMP instrument (Biologic Multichannel potentiostat). The applied amplitude of the ac voltage was 10 mV. The high frequency intercepts of the Nyquist plots were used to calculate the ionic conductivities of the separators. EIS measurements were also carried out for the LTO/Li cells with different separators following the same testing protocols. The cyclic voltammetric measurements were performed on the same VMP instrument using a potential scan rate of 0.1 mV s$^{-1}$ for all cells. The galvanostatic cycling, including the rate tests, on the Li/PRA and LTO/Li cells with different separators were performed on an Arbin instrument (model BT-2042).

Author contributions

The manuscript is written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

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