Lignin as redox-targeted catalyst for the positive vanadium electrolyte

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Abstract

Vanadium Redox Flow Batteries (VRFBs) are promising candidates for large- scale energy storage applications however, there are still some obstacles that need to be overcome such as their low energy density (25-30 Wh L^{-1} for a 1.8 M electrolyte), high cost and large environmental impact due to corrosiveness and the unsustainability of vanadium. To address these challenges, we introduce lignin as a low-cost electrocatalyst and capacity booster for the positive electrolyte. Coated on a glassy carbon electrode, lignin showed electrocatalytic abilities and improved the electrochemical reversibility of the VO^{2+}/VO_2^+ redox couple significantly. In charge and discharge cycles volumetric capacities of 28 Ah L^{-1} (charge) and 23.5 Ah L^{-1} (discharge) were achieved with a 0.9 M concentrated vanadium electrolyte which surpassed the maximum theoretical capacity of 24.1 Ah L^{-1} in the charge. This demonstrates an increase of 7.5 Ah L^{-1} and 9 Ah L^{-1} for the charge and discharge cycles, respectively, compared to

a pristine carbon felt electrode. This work showcases the noteworthy influence of lignin on vanadium and opens new possibilities for VRFB chemistry.

1 Introduction

Redox flow batteries (RFBs) are promising devices for stationary energy storage applications due to their long cycle life and their decoupled system which enables independent scaling of energy and power [1]–[3]. Among various RFBs, vanadium redox flow batteries (VRFBs) have received increasing attention due to their ability of large-scale energy storage in the range of MW/MWh [4]. However, their utilization is still affected by limiting factors like the high cost of vanadium, a narrow operating temperature range (10-40°C) and a low energy density (19-38 Wh L^{-1} with a commercial 1.5 - 2.0 M concentrated vanadium electrolyte) [3], [5], [6]. The latter issue is mainly caused by polarization losses due to high overpotentials and subsequent hydrogen and oxygen evolution at the electrodes during the charge process. Various studies have aimed at improving the reaction kinetics at the electrodes and increase the electrochemical activity of commonly used carbon felt (CF) electrodes by introducing electrocatalysts. The two main catalyst categories for the VRFB are metal-based catalysts like iridium, titanium or manganese oxide on carbon felt electrodes [7]–[10] and carbon-based catalysts like carbon nanofibers or carbon nanotubes [11], [12].

In this work, we propose a new catalytic method for the VO^{2+}/VO_2^+ reaction in which alkaline lignin combined with a small amount of multi walled carbon nanotubes (MWCNTs) is coated on pristine carbon felt electrodes. During the charge and discharge cycles, lignin is oxidized/reduced while it reduces/oxidizes the VO^{2+}/VO_2^+ species, thus exhibiting a capacity enhancing possibility for the positive half-cell. This concept demonstrates the prospects of modifying commercial CFs and to lower the environmental impact of VRFBs by reducing either the catholyte volume or vanadium concentration and compensating the capacity loss by introducing low cost and highly abundant lignin [13], [14]. In recent studies Vivo-Vilches et al. and Ribadeneyra et al. studied electrospun freestanding carbon materials

derived from lignin as a substitute electrode for commercial CFs for an all VRFB [15], [16]. However, they reported performances comparable to commercial CFs without an improvement in capacity. Herein, we take advantage of lignin's functionality as a redox-targeted catalyst for the $VO^{2+}/VO_2^+ +$ redox reaction. While electrochemically oxidized and reduced at the electrodes, lignin has the ability to act as a charge carrier in the positive vanadium electrolyte and leads to significant capacity enlargements in the positive compartment. Its functionality was tested via cyclic voltammetry (CV), linear sweep voltammetry (LSV) and polarization in a three-electrode system, as well as during the charge and discharge cycles in a flow cell.

2 Materials and methods

2.1 Preparation of the electrolyte

For the charge and discharge cycles, a solution of 0.9 M vanadium in 4.55 M sulphuric acid (H_2SO_4) and 0.025 M phosphoric acid (H_3PO_4) is used. The solution is prepared by diluting a commercial vanadium electrolyte (manufacturer Oxkem Limited, United Kingdom) with a total vanadium concentration of 1.8 M (50:50 ratio of V^{3+}/VO^{2+}, 4.6 M H_2SO_4 and 0.05 M H_3PO_4). To obtain 200 ml of a 0.9 M vanadium solution, 100 ml of 4.5 M H_2SO_4 was added to 100 ml of the 1.8 M electrolyte. For CV, LSV and polarization experiments, a solution of 0.45 M total vanadium (50:50 ratio of VO^{2+}/VO_2^+) is used. The solution was prepared by charging the 0.9 M vanadium solution in a laboratory flow cell (Figure S1 and Table S1) with a constant current of 15 mA cm^{-1} until a state of charge of 50% was reached. The electrolyte was then removed and further diluted with deionized water to obtain a 0.45 M vanadium solution.

2.2 Preparation of lignin coated electrodes

A lignin-based ink was prepared by mixing 5 g lignin, alkali (Sigma Aldrich) and 0.5 g graphitized multiwalled carbon nanotubes (MWCNTs, Nanografi, >99.99%). This mixture was filled in a ball mill cylinder and milled for 30 minutes at 400 rpm at 10-minute intervals. Afterwards, 8-10 ml of 1-

methyl-2-pyrrolidone (99.0%, Sigma Aldrich) was added to create a viscous ink which was stirred for 20 minutes using an ultrasonic overhead stirrer. For the CV, LSV and polarization experiments one drop of the ink (1.5 μl) was coated on a glassy carbon (GC) electrode (surface area 0.071 cm^2) using an ultramicro pipette. The surrounding of the GC electrode was covered with tape which was later removed so that the coated area was fixed to 0.071 cm^2. Afterwards, the electrode was immediately vacuum dried at 60°C for 24 h. For charge and discharge cycles in a flow cell a 3 cm × 3 cm carbon felt (CF) (Sigracell felt GFD 2.5EA) was thermally pre-treated at 400°C for 24 h, then immersed into the ink and gently dabbed on a paper towel to remove excess ink and to provide a uniform coating. Afterwards, the felt was immediately vacuum dried at 60°C for 24 h. The mass gain on the carbon felt was 0.5 g which corresponds to a lignin mass of 0.45 g.

2.3   Physical characterization

Morphological analysis of the coating was carried out by SEM with a Jeol JSM-6500F field emission electron microscope. The operating voltage of the electron beam was 15 kV and at a working distance of 16.5 cm for magnifications of ×5000, ×10000 and ×50000.

2.4   Electrochemical characterization

The CV, LSV and polarization experiments were performed in a three-electrode cell arrangement with a glassy carbon working electrode, a platinum mesh counter electrode and a Ag/AgCl (in 3.5 M KCl) reference electrode. The measurements were performed in 2 M H_2SO_4 and in a 0.45 M vanadium electrolyte (50:50 ratio of VO^{2+}/VO_2^+) which was purged with nitrogen throughout the experiments to maintain an inert atmosphere. The scans were recorded with an Ivium-n-Stat potentiostat (Multi-channel Potentiostat/Galvanostat/ZRA, Ivium Technologies B. V.) at scan rates of 5 mV s^{-1}, 10 mV s^{-1}, 20 mV s^{-1} and 50 mV s^{-1} for the CV and at rotation rates of 100, 200 500, 1000, 2000 and 3000 rpm for LSV on a rotating disc electrode (RDE). For each scan rate and rotation rate 4-5 cycles were repeated and the last or second last cycle was plotted.

Charge and discharge cycles were performed in a single filter-pressed flow cell (Table S1 and Figure S1) with thermally pre-treated carbon felt electrodes of 9 cm^2 projected area (Sigracell felt GFD 2.5EA). The half cells were separated by a Nafion NR-212 membrane. The 0.9 M vanadium electrolytes were stored in sealed beakers under a permanent nitrogen flow and pumped into the cell by a Masterflex pump (L/S Variable-Speed Digital Drive with Remote I/O, 6 to 600 rpm; 90 to 260 VAC). The flow rate was fixed at 50 mL min^{-1}. The operating temperature was maintained at 30°C. Galvanostatic charging and discharging of the cell was carried out with a Ivium-Vertex potentiostat (Vertex.One, Ivium Technologies B. V.). To avoid overcharge or deep discharge, cut-off cell voltages were set at 1.9 V for charge and 0.7 V for discharge. Between each charge and discharge cycle a 10-minutes resting period was set. The received electrolyte was preconditioned by charging to a positive (containing VO^{2+}/VO_2^+ ions) and a negative (containing V^{2+}/V^{3+} ions) electrolyte. Charge and discharge cycles were then performed with pristine carbon felt electrodes and afterwards with a lignin coated carbon felt cathode and a pristine carbon felt anode.

3 Results and discussion

3.1 Structural characterization

The SEM images show the fibers of the pristine carbon felt electrode (Figure 1a) and the coated carbon felt electrode (Figure 1b). It is visible that the coating adheres to the carbon fibers and is distributed in small conglomerates consisting of lignin and MWCNTs. Due to the good conductivity provided by the MWCNTs higher magnifications, where the nanotubes are visible, could be applied (Figure 1c).

## 3.2 Electrochemical characterization

To analyse the redox potentials and the catalytic properties of lignin, the lignin-based ink was coated on a glassy carbon electrode to perform CV and LSV experiments (Figure 2).

The electrochemical behaviour of lignin was first tested in H_2SO_4 and afterwards in the vanadium electrolyte to investigate the oxidation and re-

duction reactions of plain lignin and lignin combined with vanadium. The CV scan for lignin in H_2SO_4 (Figure 2a) showed two oxidation peaks, at 0.41 vs. Ag/AgCl V and at 0.67 V vs. Ag/AgCl and two reduction peaks at 0.34 V and 0.54 V vs. Ag/AgCl, giving $E'_0 = 0.38$ V vs. Ag/AgCl and $E'_0 = 0.61$ V vs. Ag/AgCl, respectively, which is in accordance with literature [17]–[19] and confirms that lignin possesses several functional groups for electron transfer reactions. When the lignin coated GC electrode was studied in the positive vanadium electrolyte, an increase in the current density by 4.5 mA cm^{-1} and a significant improve towards reversibility of the VO^{2+}/VO_2^+ redox reaction were observed compared to the bare GC electrode. Oxidation and reduction for the VO^{2+}/VO_2^+ species appeared at 1.23 V and 0.31 V vs. Ag/AgCl respectively, while peaks for the VO^{2+}/VO_2^+ species combined with lignin were observed at 1.05 V vs. Ag/AgCl for oxidation and 0.82 V vs Ag/AgCl for reduction. Thus, the peak-to-peak separation decreased from $\Delta E_p = 0.92$ V for VO^{2+}/VO_2^+ on bare GC to $\Delta E_p = 0.23$ V on lignin coated GC. It is considered that the redox reaction of lignin corresponds to a two-electron transfer reaction (Figure S2) while VO^{2+}/VO_2^+ is a one-electron transfer reaction. The ratio of the anodic to the cathodic peak current increased from $\frac{i_{pa}}{i_{pc}} = 0.63$ for plain vanadium to $\frac{i_{pa}}{i_{pc}} = 0.96$ for vanadium combined with lignin. From the CV curves at different scan rates in Figure 2b, the kinetic rate constants were calculated from the Tafel plots (Figure S4), giving the effective anodic and cathodic rate constants of $k_a \geq 7.6 \times 10^{-7}$ m s^{-1} and $k_c \geq 4.2 \times 10^{-6}$ m s^{-1} on bare GC (which are comparable with literature ([20]), and $k_a \geq 4.4 \times 10^{-6}$ m s^{-1} and $k_c \geq 5.1 \times 10^{-6}$ m s^{-1} on the lignin coated GC electrode. This shows an increase of one order of magnitude higher for the anodic reaction. LSV scans demonstrate that compared to the bare GC, the lignin coated GC electrode reduced the hysteresis in potential and revealed a more reversible wave for the oxidation and reduction of the VO^{2+}/VO_2^+ couple (Figure 2c and d). From the LSV curves in Figure 2d, the diffusion coefficients for the VO^{2+}/VO_2^+ species were calculated using the Levich-plot (Figure S5) and compared for both electrodes. With $D_a = 6.5 \times 10^{-11}$ m^2 s^{-1} for oxidation and $D_c = 6.9 \times 10^{-11}$ m^2 s^{-1} for reduction, the diffusion coefficients for VO^{2+}/VO_2^+ on the lignin coated GC electrode are in the same range as for bare GC (Table S2) and correspond to the literature values reported for the vanadium electrolyte [21].
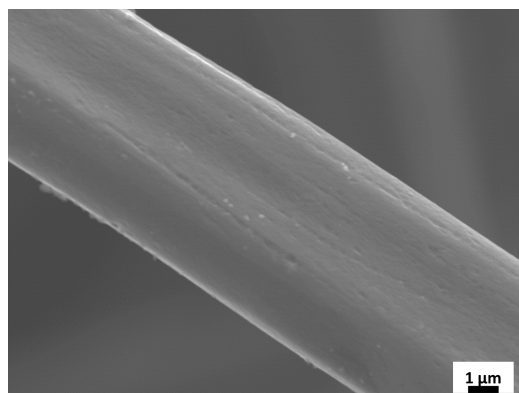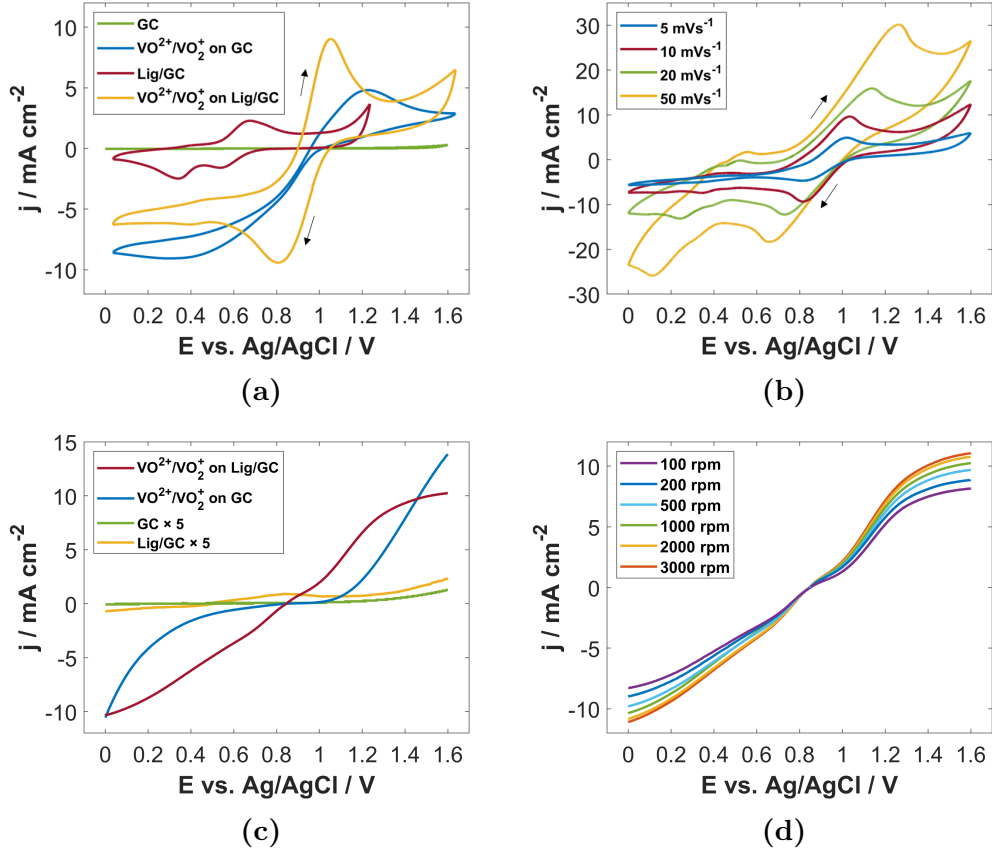
(a)
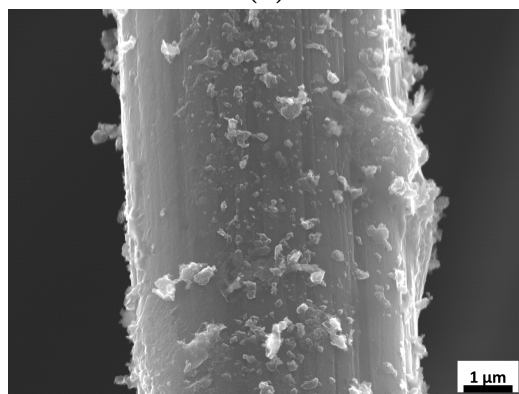
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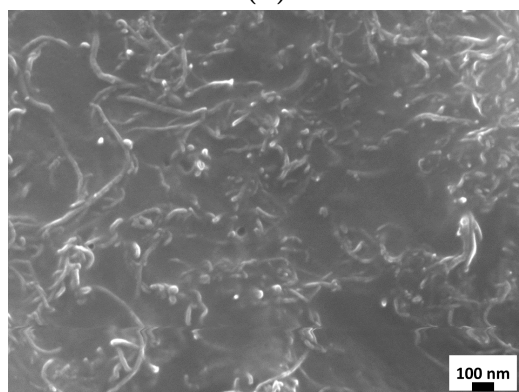
(c)

Figure 1: SEM images of the bare CF electrode at a magnification of ×5000 (a) and the lignin coated GC electrode at a magnification of ×10000 (b) and ×50000 (c).

Figure 2: (a) Cyclic voltammograms on a bare GC electrode and a lignin coated GC electrode measured in 2 M H_2SO_4 as reference solution, and in 0.45 M positive vanadium electrolyte at a scan rate of 10 mV s^{-1}. (b) Cyclic voltammograms on a lignin coated GC electrode in 0.45 M positive vanadium electrolyte at different scan rates (5 mV s^{-1}, 10 mV s^{-1}, 20 mV s^{-1}, 50 mV s^{-1}). (c) LSV curves on a lignin coated GC rotating disc electrode and on a bare GC rotating disc electrode measured in 2 M H_2SO_4 as reference solution, and in a 0.45 M positive vanadium electrolyte at a rotation speed of 1000 rpm and a scan rate of 10 mv s^{-1}. d) LSV curves on a lignin coated GC RDE electrode in 0.45 M positive vanadium electrolyte at different rotating speeds (100, 200, 500, 1000, 2000 and 3000 rpm) and a scan rate of 10 mV s^{-1}.

As seen in Figure 3a, the lignin coated GC electrode shows lower polarization than the GC for current densities above 7 mA cm^{-2}, where the bare GC electrode tends towards higher overpotentials due to the OER with increasing current density.

The lignin coated CF electrode was tested in a flow cell to examine the possibility of a capacity enhancing effect. Charge and discharge cycles were performed in a flow cell configuration maintaining volumes of 80 ml in the negative electrolyte reservoir and 40 ml in the positive electrolyte reservoir so that the catholyte volume is only half of the anolyte volume. The reason to use half volume in the positive electrolyte was to evaluate if the lignin/MWCNTs would be able to compensate for the lower catholyte volume and therefore for the lower electroactive species available. This configuration provides a capacity limitation by the positive half-cell and enables room for a visible capacity increase.
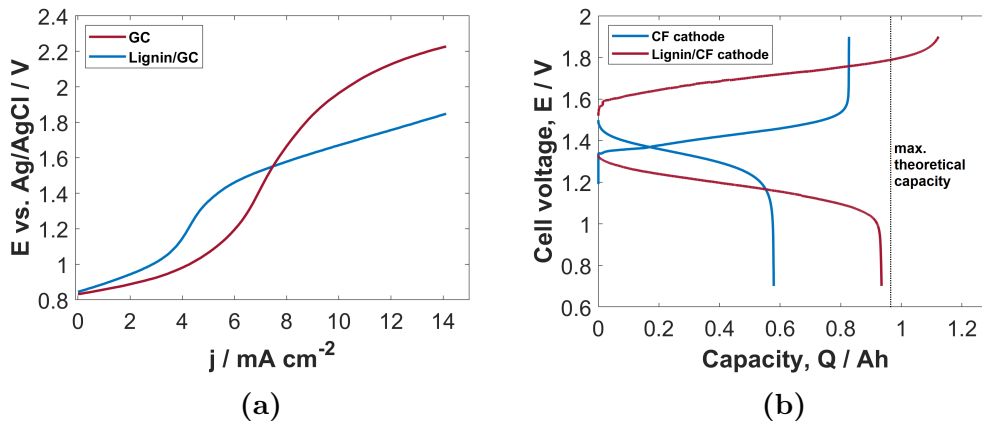
Figure 3: (a) Polarization curves on a lignin coated GC electrode and on a bare GC electrode for comparison in a 0.45M positive vanadium electrolyte. (b) Voltage profile of a VRFB with a lignin coated carbon felt cathode and with a pristine carbon felt cathode for comparison. In both cells, the anodes were pristine CFs and the anolyte volume was 80 ml, while the catholyte volume was 40 ml so that the capacity was limited by the positive half-cell.

Figure 3b demonstrates the cell voltage profiles for a flow cell with pristine CF electrodes in both half-cells (blue line) and with a pristine CF electrode in the negative half-cell and a lignin coated CF electrode in the positive half-cell. To analyze the performance of the flow cell, the capacity values were
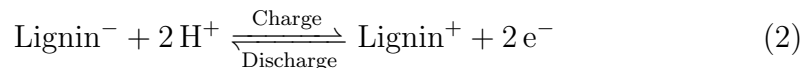
compared with the theoretical volumetric capacity which could be achieved for this system when 100% charged. This can be calculated using Faraday's law (1).

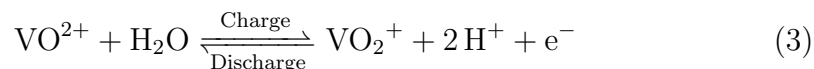$$Q = \frac{m}{M} \cdot F \cdot z \qquad (1)$$

F is Faraday's constant (96485 C mol^{-1}), z the number of electrons interchanged, and m and M are mass and molar mass of vanadium. The calculation for a 0.9 M concentrated electrolyte with a catholyte volume of 40 ml gives a maximum theoretical capacity of 0.965 Ah. The cell with pristine CF electrodes reached a charge capacity of 0.82 Ah and a discharge capacity of 0.58 Ah. Considering that the electrolyte had an initial state of charge (SoC) of 0-5% measured by OCV, the cell was charged to a SoC of 86% and discharged to a SoC of 26%, obtaining a Coulombic efficiency of 70%.

After replacing the pristine CF with a lignin coated CF cathode, an increase in the cell voltage for the charge and a decrease of the cell voltage for the discharge was observed which could be caused by the denser and more rigid texture of the coated CF. Since it is less porous than the pristine CF, it causes a higher internal resistance.
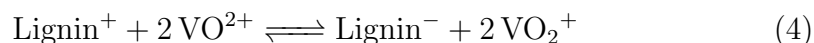
However, even at a higher cell voltage a capacity increase by 0.41 Ah for the charge was observed. For the discharge cycle, a capacity rise by 0.35 Ah compared to the pristine CF cathode was obtained. This led to capacity values of 1.12 Ah (28 Ah L^{-1}) after charge and 0.94 Ah (23.5 Ah L^{-1}) after discharge which shows that the charge surpassed the theoretical capacity for 100% SoC for the 40 ml electrolyte by 0.16 Ah (an increase of 16.4%). Thus, lignin not only has the functionality as redox-targeted catalyst but also acts as an additional charge carrier in the electrolyte. It is known from the literature that vanadium is a catalyst for C-O and C-C cleavage of lignin [22], [23]. Thus, it oxidizes lignin while it is reduced. Regarding the redox potential of lignin, according to literature the only estimation has been done indirectly [19]. Thus, for the reaction in the vanadium electrolyte the redox potential could only be determined indirectly from the calculated formal potential (E'_0 = 0.61 V vs. Ag/AgCl) and from estimated/calculated literature values [17]–[19]. Since the potential is strongly dependent on the pH, a potential range of E_0 = 0.6 - 0.9 V vs. SHE is assumed. The electrochemical redox reactions occurring at the positive electrode are shown in Equations 2 - 4:

$$\text{Lignin}^- + 2\,\text{H}^+ \xrightleftharpoons[\text{Discharge}]{\text{Charge}} \text{Lignin}^+ + 2\,\text{e}^- \tag{2}$$

$$E_0 \text{ (lignin)} = 0.6\text{ - }0.9 \text{ V vs. SHE}$$

$$\text{VO}^{2+} + \text{H}_2\text{O} \xrightleftharpoons[\text{Discharge}]{\text{Charge}} \text{VO}_2{}^+ + 2\,\text{H}^+ + \text{e}^- \tag{3}$$

$$E_0 \text{ (VO}^{2+}/\text{VO}_2^+) = 1.00 \text{ V vs. SHE}$$

$$\text{Lignin}^+ + 2\,\text{VO}^{2+} \rightleftharpoons \text{Lignin}^- + 2\,\text{VO}_2{}^+ \tag{4}$$

During the charge, it is assumed that the reaction starts with the oxidation of lignin due to its lower redox potential, which is accompanied by the release of H^+ (Eq. 2). Once lignin is oxidized and predominant the electrode surface, the reaction is driven towards the reduction of lignin by the VO^{2+} ions so that lignin remains unchanged (Eq. 4). Additionally, VO^{2+} ions are electrochemically oxidized to VO_2^+ ions (Eq. 3). The proof of the redox reaction between lignin and $\text{VO}^{2+}/\text{VO}_2^+$ can be visualized in a spontaneous reaction test (Figure S6). The direction of a spontaneous reaction seems to be leading to one direction only - the oxidation of lignin. However, CV, LSV and the charge and discharge cycles implicate that when applied at the electrode the a reversibility of the reaction is possible. In this way, lignin is re-oxidized again at the electrodes which explains the obtained increase in capacity surpassing the theoretical possible capacity for the vanadium species.

Since the theoretical capacity of lignin is not known from literature, a relation between mass of applied lignin and expected capacity increase needs further investigation. Figure 4 shows the voltage profiles and the capacities and efficiencies over the first 10 cycles. For the first two cycles, an energy efficiency of 74%, a Coulombic efficiency of 84% and voltage efficiency of 88% were achieved with the modified electrode. While with the pristine electrode the efficiencies were 65%, 70% and 93%, respectively. It is visible that the charge and discharge capacities were stable for the first two cycles but dropped constantly for more cycles. This may be caused by the slow dissolution of the coating in the electrolyte. Therefore, the amount of lignin applied to the electrode and the stability of the coating needs to be further investigated to improve its durability.
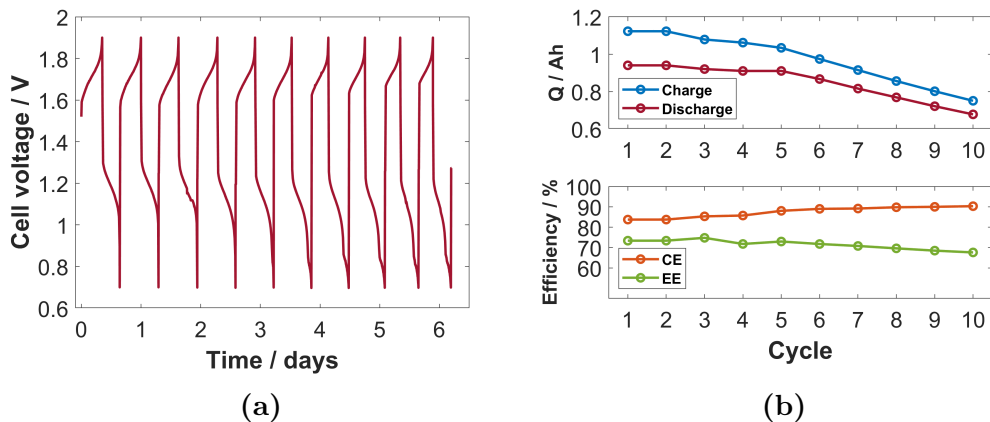
Figure 4: Charge and discharge cycles with pristine CF as a negative electrode and lignin coated CF as a positive electrode for a 80 ml negative and 40 ml positive electrolyte reservoir. (a) Voltage profile for 10 cycles. (b) Charge and discharge capacity, Coulombic efficiency (CE) and energy efficiency (EE) for 10 cycles.

4   Conclusions

We studied the effect of lignin combined with MWCNTs coated on carbon electrodes in a positive vanadium electrolyte. The electrocatalytic activity towards the VO^{2+}/VO_2^+ couple was examined in a three-electrode arrangement for cyclic voltammetry, linear sweep voltammetry and polarization curves, and in a single filter-pressed flow cell for charge and discharge cycles. The results show:

- The reaction kinetics and the reversibility for the VO^{2+}/VO_2^+ redox reactions were greatly improved when lignin was deposited on the electrode.

- The peak-to-peak separation was reduced from ΔE_p 0.92 V vs. Ag/AgCl on bare GC to ΔE_p 0.23 V vs. Ag/AgCl on lignin coated GC, while the peak current ratio increased from $\frac{i_{pa}}{i_{pc}} = 0.63$ for plain vanadium to $\frac{i_{pa}}{i_{pc}} = 0.96$ for vanadium combined with lignin. Thus, lignin increased the reversibility of the vanadium redox reactions.

- The effective anodic and cathodic kinetic rate constants increased from

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$k_a \geq 7.6 \times 10^{-7}$ m s^{-1} and $k_c \geq 4.2 \times 10^{-6}$ m s^{-1} on bare GC to $k_a \geq 4.4 \times 10^{-6}$ m s^{-1} and $k_c \geq 5.1 \times 10^{-6}$ m s^{-1} on the lignin GC electrode.

- LSVs showed that compared to bare GC the lignin coated electrode suppressed the OER.

These results are remarkable for the charge and discharge cycles and revealed a significant enhancement in charge storage capacity which surpassed the maximum theoretical volumetric capacity for the electrolyte by 16.4%, indicating that lignin not only acts as an electrocatalyst but also as an additional charge carrier. Its application in a flow cell needs to be studied in more detail to be improved for an optimal operation and a longer stability. The durability of the coated electrode as well as the endurance of lignin in the electrolyte environment need further investigation. However, it is expected that this concept will be valid for an improvement in the commercial application of VRFBs.

Acknowledgements

A   Supplementary Information

References

[1]   G. L. Soloveichik, "Flow batteries: Current status and trends," *American Chemical Society*, vol. 115, pp. 11 533–11 558, 2015. DOI: `https://doi.org/10.1021/cr500720t`.

[2]   M. Mohamed, S. Sharkh, and F. Walsh, "Redox flow batteries for hybrid electric vehicles: Progress and challenges," *2009 IEEE Vehicle Power and Propulsion Conference*, pp. 551–557, 2009. DOI: `10.1109/VPPC.2009.5289801`.

[3] J. Noack, N. Roznyatovskaya, T. Herr, and P. Fischer., "Die Chemie der Redox-Flow-Batterien," *Angewandte Chemie*, vol. 127, pp. 9912–9947, 2015. DOI: https://doi.org/10.1002/ange.201410823.

[4] Z. Abdin and K. R. Khalilpour, "Single and polystorage technologies for renewable-based hybrid energy systems," *Polygeneration with Polystorage: For Chemical and Energy Hubs*, pp. 77–131, 2018.

[5] C. Ding, H. Zhang, X. Li, T. Liu, and F. Xing, "Vanadium flow battery for energy storage: Prospects and challenges," *Journal of Physical Chemistry Letters*, vol. 4, pp. 1281–1294, 2013. DOI: https://doi.org/10.1021/jz4001032.

[6] F. Rahman and M. Skyllas-Kazacos, "Vanadium redox battery: Positive half-cell electrolyte studies," *Journal of Power Sources*, vol. 189, pp. 1212–1219, 2009. DOI: https://doi.org/10.1016/j.jpowsour.2008.12.113.

[7] M. Taş and G. Elden, "A comprehensive review of carbon-based and metal-based electrocatalysts in the vanadium redox flow battery," *Energy Storage*, vol. 4(2), e265, 2022. DOI: https://doi.org/10.1002/est2.265.

[8] W.H.Wang and X.D.Wang, "Investigation of ir-modified carbon felt as the positive electrode of an all-vanadium redox flow battery," *Electroquimica Acta*, vol. 52, pp. 6755–6762, 2007. DOI: https://doi.org/10.1016/j.electacta.2007.04.121.

[9] Y. Ji, J. L. Li, and S. F. J. Li, "Synergistic effect of the bifunctional polydopamine-Mn_3O_4 composite electrocatalyst for vanadium redox flow batteries," *Journal of Materials Chemistry A*, vol. 5, pp. 15 154–15 166, 2017. DOI: https://doi.org/10.1039/C7TA03922K.

[10] G. Wei, M. Jing, X. Fan, J. Liu, and C. Yan, "A new electrocatalyst and its application method for vanadium redox flow battery," *Journal of Power Sources*, vol. 28, pp. 81–86, 2015. DOI: https://doi.org/10.1016/j.jpowsour.2015.04.041.

[11] W. Li, J. Liu, and C. Yan, "Multi-walled carbon nanotubes used as an electrode reaction catalyst for VO^{2+}/VO_2^+ for a vanadium redox flow battery," *Carbon*, vol. 49, pp. 3463–3470, 2011. DOI: https://doi.org/10.1016/j.carbon.2011.04.045.

[12] G. Wei, C. Jia, J. Liu, and C. Yan, "Carbon felt supported carbon nanotubes catalysts composite electrode for vanadium redox flow battery application," *Journal of Power Sources*, vol. 220, pp. 185–192, 2012. DOI: https://doi.org/10.1016/j.jpowsour.2012.07.081.

[13] L. Hodásová, M. Jablonský, A. Škulcová, and A. Ház, "Lignin, potential products and their market value," *Wood Research*, vol. 60, pp. 973–986, 2015.

[14] I. Surina, M. Jablonský, A. Ház, A. Sladková, A. Briškárová, F. Kačík, and J. Šima, "Characterization of Non-wood Lignin Precipitated with Sulphuric Acid of Various Concentrations," *BioResources*, vol. 10, pp. 1408–1423, 2015.

[15] V. Vilches, A. Celzard, V. Fierro, I. Devin-Ziegler, N. Brosse, A. Dufour, and M. Etienne, "Lignin-based carbon nanofibers as electrodes for vanadium redox couple electrochemistry," *Physical Chemistry Chemical Physics*, vol. 9, pp. 1–106, 2019. DOI: https://doi.org/10.3390/nano9010106.

[16] M. Ribadeneyra, L. Grogan, H. Au, *et al.*, "Lignin-derived electrospun freestanding carbons as alternative electrodes for redox flow batteries," *Carbon*, vol. 157, pp. 847–856, 2020. DOI: https://doi.org/10.1016/j.carbon.2019.11.015.

[17] G. Milczarek, "Preparation and characterization of a lignin modified electrode," *Electroanalysis*, vol. 19(13), pp. 1411–1414, 2007. DOI: https://doi.org/10.1002/elan.200703870.

[18] Y. Dessie and S. Admassie, "Electrochemical study of conducting polymer/lignin composites," *Orient. J. Chem.*, vol. 29(4), pp. 1359–1369, 2013. DOI: http://dx.doi.org/10.13005/ojc/290411.

[19] M. N. Muraleedharan, D. Zouraris, A. Karantonis, E. Topakas, M. Sandgren, U. Rova, P. Christakopoulos, and A. Karnaouri, "Effect of lignin fractions isolated from different biomass sources on cellulose oxidation by fungal lytic polysaccharide monooxygenases," *Biotechnol. Biofuels*, vol. 11, p. 296, 2018. DOI: https://doi.org/10.1186/s13068-018-1294-6.

[20] N. Roznyatovskaya, J. Noack, K. Pinkwart, and J. Tübke, "Aspects of electron transfer processes in vanadium redox-flow batteries," *Current Opinion in Electrochemistry*, vol. 19, pp. 42–48, 2020. DOI: `https://doi.org/10.1016/j.coelec.2019.10.003`.

[21] F. Chen, H. Chen, Q. Sun, J. Liu, C. Yan, and Q. Liu, "Electron-transfer kinetics of V(IV)/V(V) and V(II)/V(III) couples for different state of charge," *Int. J. Electrochem. Sci.*, vol. 10, pp. 725–736, 2015.

[22] Y. Jiang, L. Yan, H. Yu, Q. Zhang, and Y. Fu, "Mechanism of vanadium-catalyzed selective C-O and C-C cleavage of lignin model compound," *ACS Catalysis*, vol. 7, pp. 4399–4410, 2016. DOI: `https://doi.org/10.1021/acscatal.6b00239`.

[23] Y. Ma, Z. Du, J. Liu, F. Xia, and J.Xu, "Selective oxidative C–C bond cleavage of a lignin model compound in the presence of acetic acid with a vanadium catalyst," *Royal Society of Electrochemistry*, vol. 17, pp. 4968–4973, 2015. DOI: `https://doi.org/10.1039/C5GC00645G`.