

Supplementary Information

Lignin as redox-targeted catalyst for the positive vanadium electrolyte

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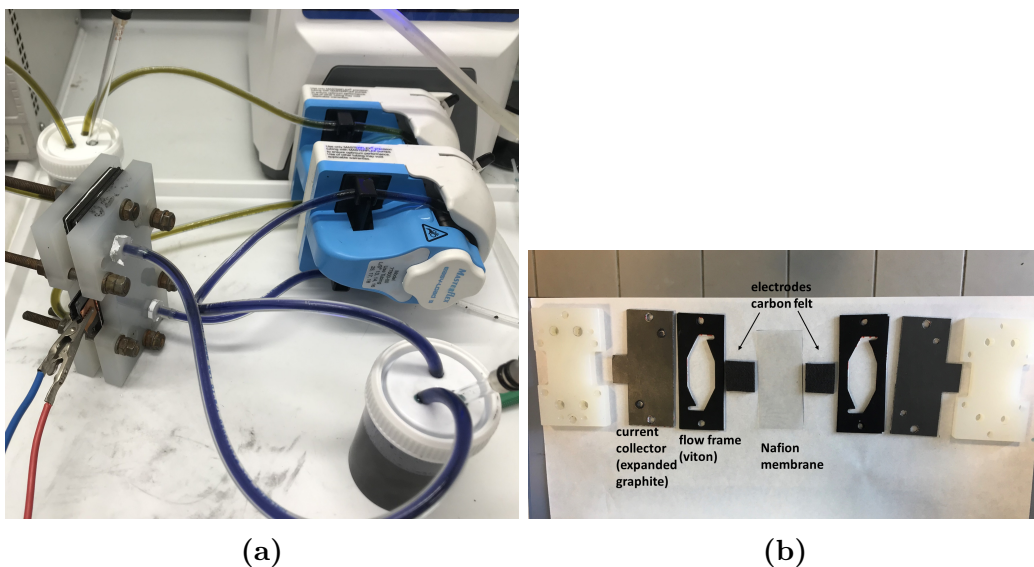


Figure S1: a) Set-up for the charge and discharge cycles with a single flow cell. b) Compartments of the flow cell.

| Small cell operating conditions | Value |
|---------------------------------|----------------------------------|
| Thickness of flow frame | 2 mm |
| Tubing inner diameter | 3.175 mm |
| Tubing outer diameter | 6.35 mm |
| Volumetric Flow, Q | 50 ml/min |
| Temperature | 303.15 K |
| Electrodes - GFD2.5A | Value |
| Height (y) | 3 cm |
| Width (x) | 3 cm |
| Thickness (z) | 2.5 mm |
| Compression rate | 20 % |
| Membrane Nafion 212 | Value |
| Thickness | 50.8 μm |
| Ionic conductivity | 3.3×10^{-4} S/cm (25°C) |

Table S1: Parameters of the single VRFB cell

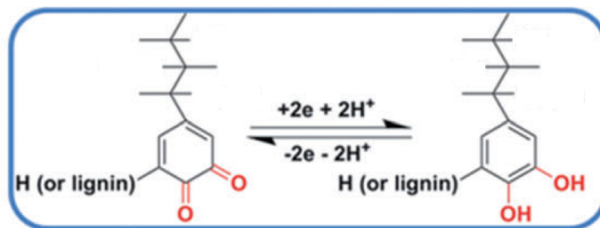


Figure S2: Expected oxidation and reduction of lignin. The redox reaction is considered to be a two-electron transfer.

For a comparison of the CV and LSV scans on the lignin electrode (Figure 2), an evaluation at different scan rates/rotation speeds was also carried out for the experiments performed on a bare GC electrode in a 0.45 M concentrated positive vanadium electrolyte (Figure S3).

From the CVs at different scan rates (Figure 2b for lignin/GC electrode and Figure S3a for the bare GC electrode) the heterogeneous kinetic rate constants k_a and k_c were calculated using Equation (S1) for the peak current i_p (S5)

$$i_p = 0.227nFACk \exp \left[-\frac{\alpha nF}{RT} (E_p - E_0) \right] \quad (\text{S5})$$

where i_p is the peak current, A is the electrode surface area, F is Faraday's constant, C is the bulk concentration, α is the transfer coefficient and n is the number of electrons involved in the redox reaction. A plot of $\ln(i_p)$ vs. $(E_p -$

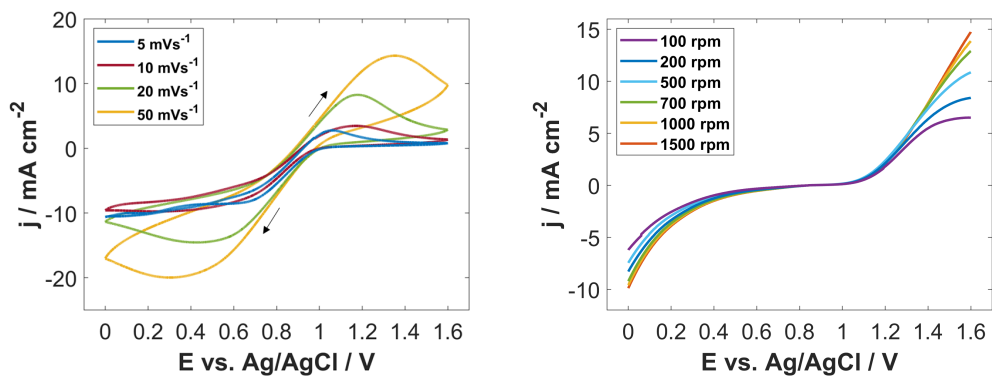


Figure S3: (a) CVs at different scan rates on a bare GC electrode in 0.45 M positive vanadium electrolyte. (b) LSVs at different rotation speeds and at a constant scan rate of 10 mV s^{-1} on a bare GC electrode in 0.45 M positive vanadium electrolyte.

E_0) determined from different scan rates results to a slope of $-(\alpha nF/RT)$ and an y-intercept which is proportional to k . Figure S4a and b demonstrate these plots for the reaction on the GC electrode and on the lignin/GC electrode. The rate constants k_a and k_c are presented in Table S2.

| Electrode | $k_a / \text{m s}^{-1}$ | $k_c / \text{m s}^{-1}$ | $D_a / \text{m}^2 \text{ s}^{-1}$ | $D_c / \text{m}^2 \text{ s}^{-1}$ |
|-----------|-------------------------|-------------------------|-----------------------------------|-----------------------------------|
| GC | 7.6×10^{-7} | 4.2×10^{-6} | 1.3×10^{-11} | 2.5×10^{-11} |
| Lignin/GC | 4.4×10^{-6} | 5.1×10^{-6} | 6.5×10^{-11} | 6.9×10^{-11} |

Table S2: Calculated values for anodic and cathodic kinetic rate constants and anodic and cathodic diffusion coefficients for the $\text{VO}^{2+}/\text{VO}_2^+$ reaction on a GC electrode and on a lignin coated GC electrode.

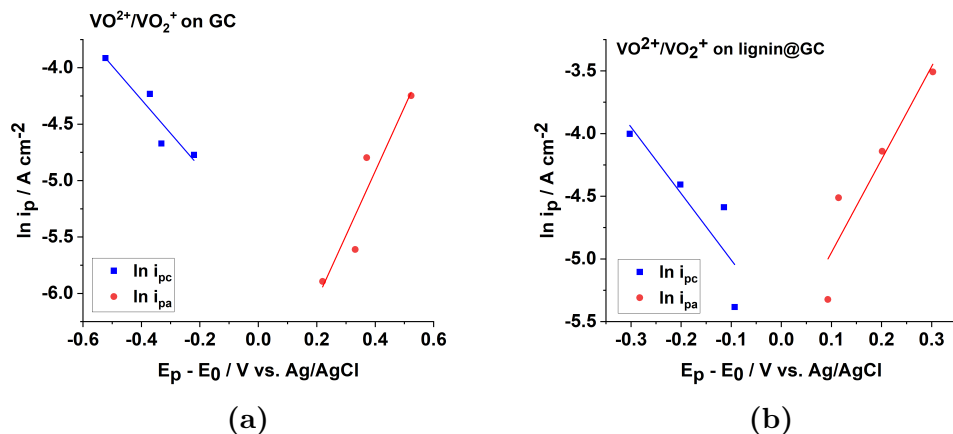


Figure S4: a) Plot of $\ln i_p$ vs. $E_p - E_0$ for the $\text{VO}^{2+}/\text{VO}_2^+$ couple on a bare GC. b) Plot of $\ln i_p$ vs. $E_p - E_0$ for the $\text{VO}^{2+}/\text{VO}_2^+$ couple on a lignin coated GC.

Furthermore, from the RDE scans at different rotation speeds (Figure 2d for the lignin coated GC and Figure S3b for the bare GC) the diffusion coefficients were determined by the Levich-equation where the limiting current density i_L is described by Equation (S2) Bard₂₀₀₁book :

$$i_L = 0.62nFD^{2/3}\vartheta^{-1/6}\omega^{1/2}c_0 \quad (\text{S6})$$

where n is the number of electrons involved in the redox reaction, F is Faraday's constant, D is the diffusion coefficient, ϑ is the viscosity of the electrolyte, ω is the angular velocity of rotation and c is the bulk concentration. From this equation and the Koutecky-Levich plots for different rotation rates, the diffusion coefficients D_a and D_c were calculated for the reactions of $\text{VO}^{2+}/\text{VO}_2^+$ on the bare GC and the lignin coated GC electrode. The values are presented in Table S2.

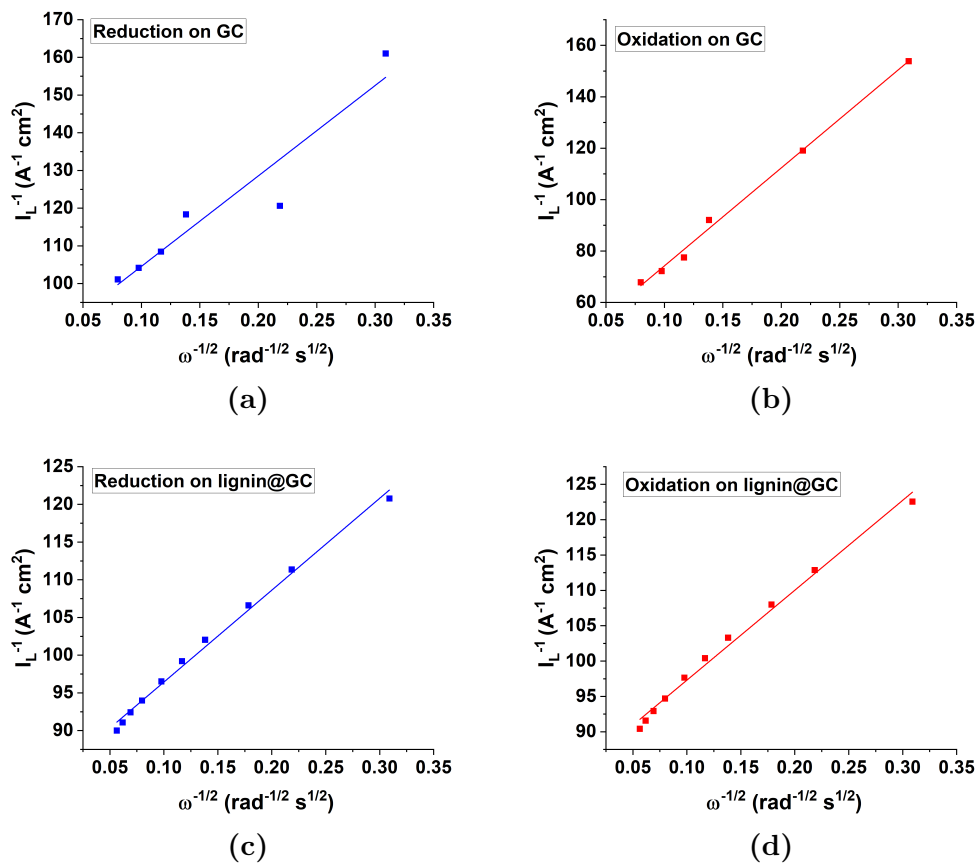


Figure S5: Plots of i_L vs. $\omega^{1/2}$ for a) the reduction of VO_2^+ to VO^{2+} on a bare GC, b) the oxidation of VO^{2+} to VO_2^+ (b) on a bare GC, c) the reduction of VO_2^+ to VO^{2+} on a lignin coated GC electrode and d) the oxidation of VO^{2+} to VO_2^+ on a lignin coated electrode.

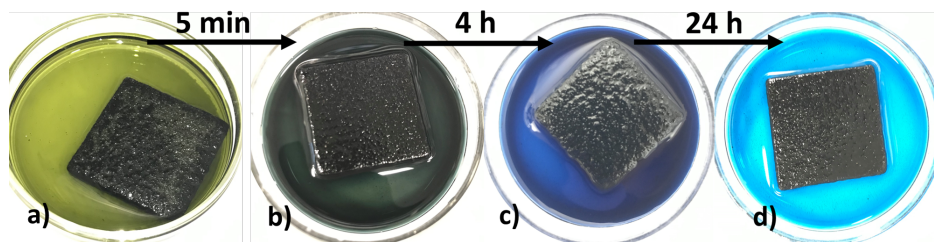


Figure S6: Spontaneous redox reaction between lignin (coated on the CF) and the $\text{VO}_2^+/\text{VO}_2^+$ species in the positive electrolyte. The reaction becomes visible through a colour change of the electrolyte.

Figure S6 demonstrates the proof of the redox reaction between lignin and $\text{VO}_2^+/\text{VO}_2^+$ in a spontaneous reaction test. The lignin coated CF was placed in a highly charged positive electrolyte and stored at room temperature. The pictures represent the changes in the SoC of the electrolyte. Figure S6a shows a 95% charged positive electrolyte (yellow/greenish color, 95:5 ratio of $\text{VO}_2^+/\text{VO}^{2+}$). An immediate colour change was visible to dark green, indicating that the reduction of VO_2^+ ions has started (Figure S6b). After 4 hours, the electrolyte had turned dark blue, corresponding to a discharged positive electrolyte at a SoC of $\sim 10\%$ (Figure S6c). The complete colour change to light blue took another 24 hours (Figure S6d). Thus, the reaction kinetics get slower with decreasing concentration of VO_2^+ ions. The light blue colour in the last picture indicates the oxidation state IV *Skyllas_Bbook2013, therefore it proves that all VO_2^+ were reduced to VO^{2+} .*

References

- [1] Bard, A. J. and Faulkner, L. R., *Electrochemical Methods: Fundamentals and Applications*, Wiley 2nd Edition (2001)
- [2] M.Skyllas-Kazacos and C.Menictas and T.Lim, *Redox flow batteries for medium- to large-scale energy storage in "Electricity Transmission, Distribution and Storage Systems"*, Woodhead Publishing Series in Energy 1 (2013) 398-441.