

Supplementary Materials:

# Characterization of Dimeric Vanadium Uptake and Species in Nafion™ and Novel Membranes from Vanadium Redox Flow Batteries Electrolytes

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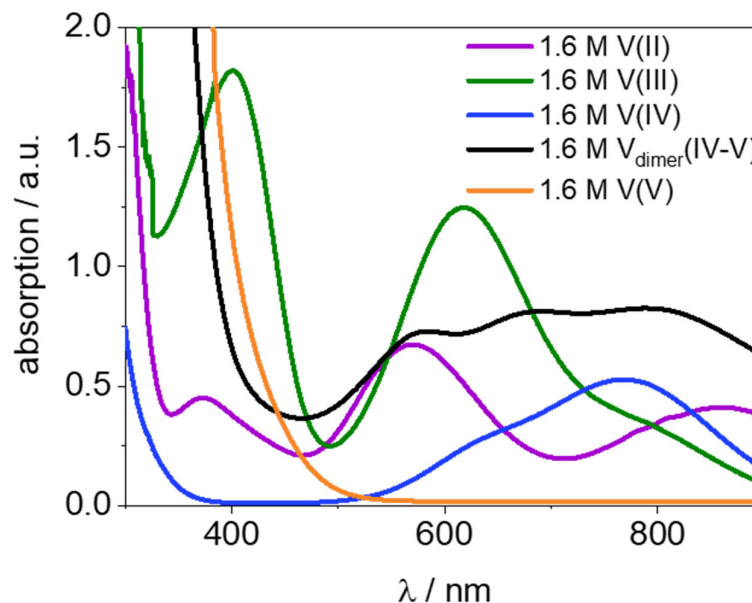
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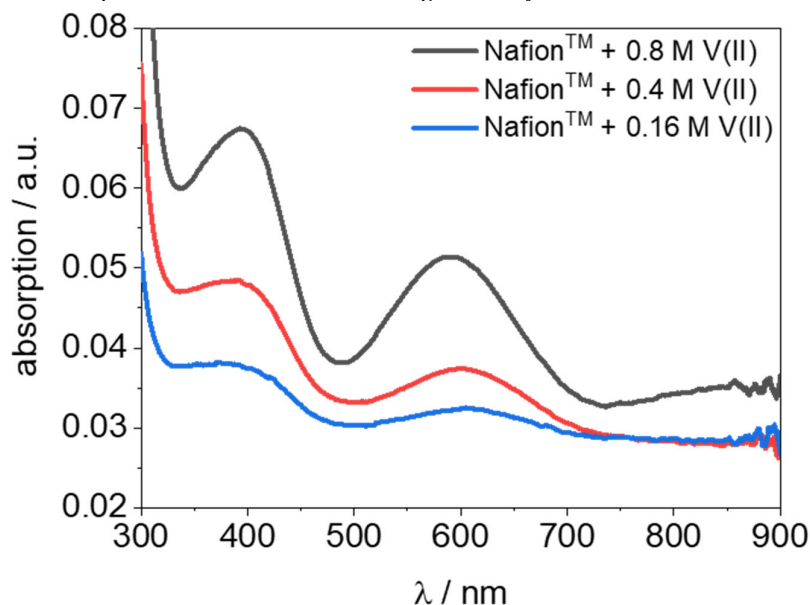
In Figure S1, the UV/VIS spectra of 1.6 M V(II), 1.6 M V(III), 1.6 M V(IV), 1.6 M V(IV/V), and 1.6 M V(V) electrolyte are shown. The V(II) and V(III) electrolyte were analyzed using a 1 mm cuvette and the V(IV), V(IV/V), and V(V) electrolyte using a 0.1 mm flow through cuvette. The data are in agreement with the literature [1,2].



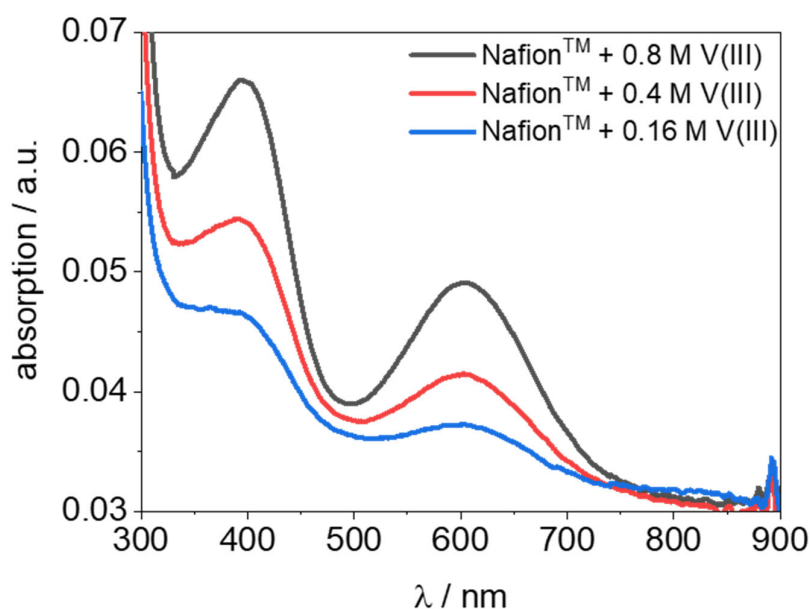
**Figure S1.** UV/VIS spectra of 1.6 M V(II), 1.6 M V(III), 1.6 M V(IV), 1.6 M V(IV/V), and 1.6 M V(V) electrolyte.

In Figure S2 to S6, UV/VIS spectra of Nafion<sup>TM</sup> hydrated with either V(II), V(III), V(IV), V(IV/V), and V(V) electrolyte with the concentrations 0.8 M, 0.4 M and 0.16 M are shown. As discussed in the result section, UV/VIS spectra of Nafion<sup>TM</sup> hydrated with lower concentrations of vanadium provide good data for the speciation.

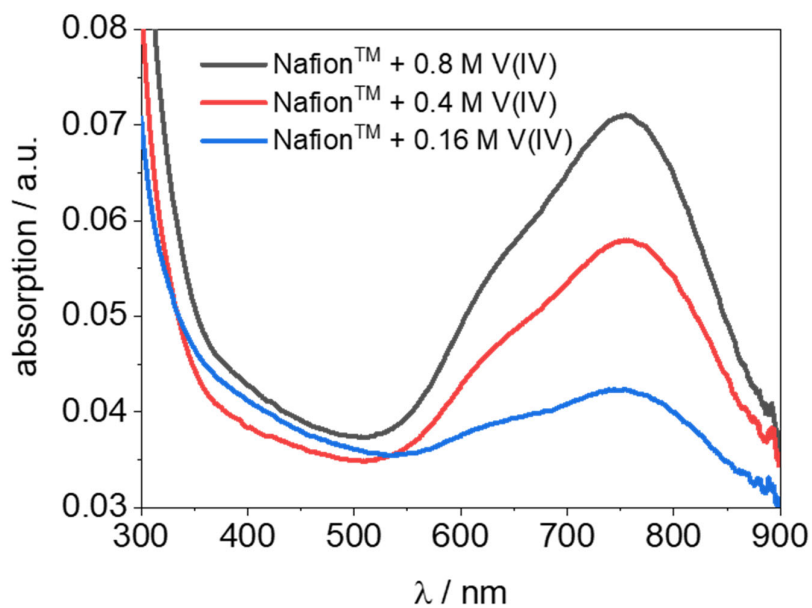
The same measurements were applied to the PVDF-based membrane. It was evident that the PVDF-based membrane hydrated in 0.8 M vanadium electrolyte provides not evaluable spectra anymore. Considering the uptake of the PVDF-based membrane compared to Nafion<sup>TM</sup> must be significantly lower.



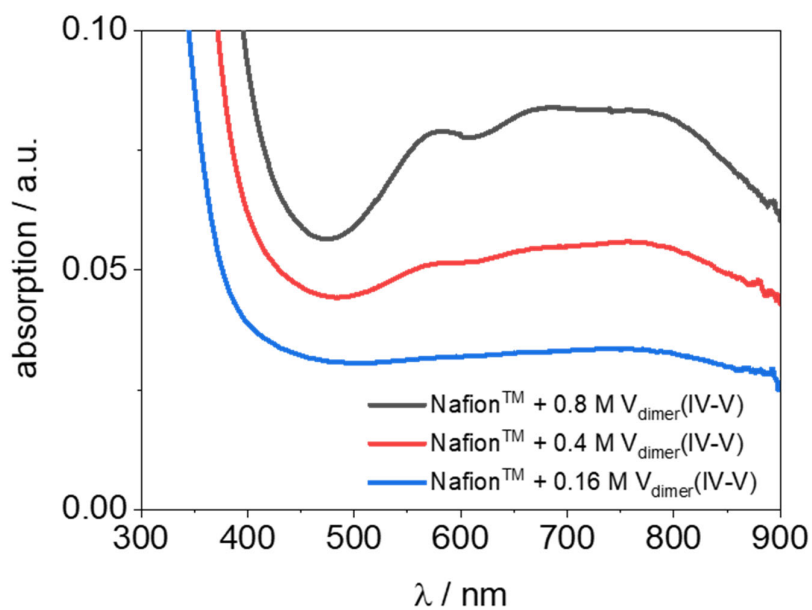
**Figure S2.** UV/VIS spectra of Nafion<sup>TM</sup> hydrated with 0.8 M, 0.4 M, and 0.16 M V(II) electrolyte.



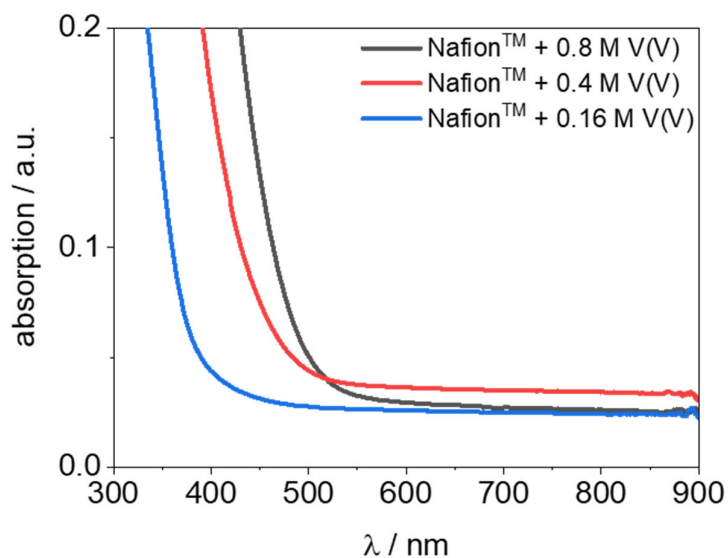
**Figure S3.** UV/VIS spectra of Nafion<sup>TM</sup> hydrated with 0.8 M, 0.4 M, and 0.16 M V(III) electrolyte.



**Figure S4.** UV/VIS spectra of Nafion<sup>TM</sup> hydrated with 0.8 M, 0.4 M, and 0.16 M V(IV) electrolyte.

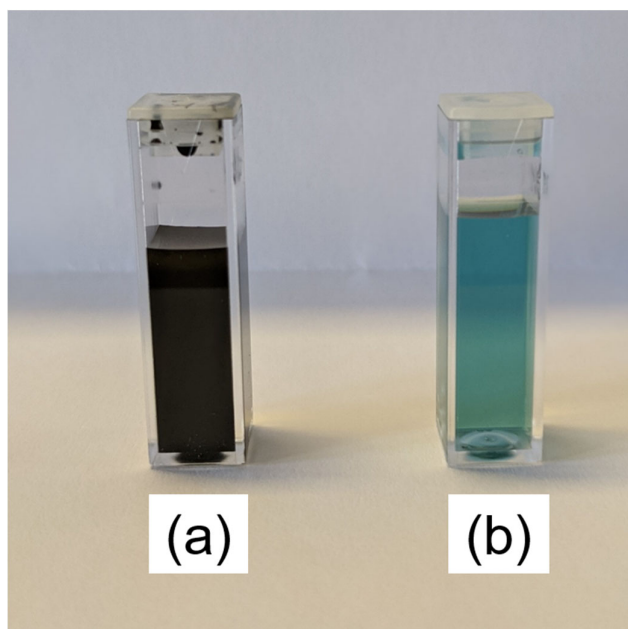


**Figure S5.** UV/VIS spectra of Nafion<sup>TM</sup> hydrated with 0.8 M, 0.4 M, and 0.16 M V(IV)/V electrolyte.



**Figure S6.** UV/VIS spectra of Nafion<sup>TM</sup> hydrated with 0.8 M, 0.4 M, and 0.16 M V(V) electrolyte.

In Figure S7, a photograph of V(IV/V) electrolyte is shown with the concentrations 1.6 M (a) and 0.1 M (b).



**Figure S7.** Photograph of V(IV/V) electrolyte with the concentrations 1.6 M (a) and 0.1 M (b).

## References

1. Buckley, D.N.; Gao, X.; Lynch, R.P.; Quill, N.; Leahy, M.J. Towards Optical Monitoring of Vanadium Redox Flow Batteries (VRFBs): An Investigation of the Underlying Spectroscopy. *J. Electrochem. Soc.* **2014**, *161*, A524–A534, doi:10.1149/2.023404jes.
2. Petchsingh, C.; Quill, N.; Joyce, J.T.; Eidhin, D.N.; Oboroceanu, D.; Lenihan, C.; Gao, X.; Lynch, R.P.; Buckley, D.N. Spectroscopic Measurement of State of Charge in Vanadium Flow Batteries with an Analytical Model of V<sup>IV</sup>-V<sup>V</sup> Absorbance. *J. Electrochem. Soc.* **2016**, *163*, A5068–A5083, doi:10.1149/2.0091601jes.