Revealing the Pseudocapacitance Charge Storage Mechanism of Sulfur-Doped Carbon Supercapacitors in Non-Aqueous Electrolyte through *in situ* EPR

Tobias Neff[1,2#], Friedrich Stemmler[3#], Leonhard Kolb[2], Joris van Slageren[3], Anke Krueger[1*]

[1]Institute of Organic Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany, [2]Institute for Organic Chemistry, Julius-Maximilian University Würzburg, Am Hubland, 97074 Würzburg, Germany, [3]Institute of Physical Chemistry, Pfaffenwaldring 55, 70569 Stuttgart, Germany

#equal contribution, *anke.krueger@oc.uni-stuttgart.de

Supporting Information

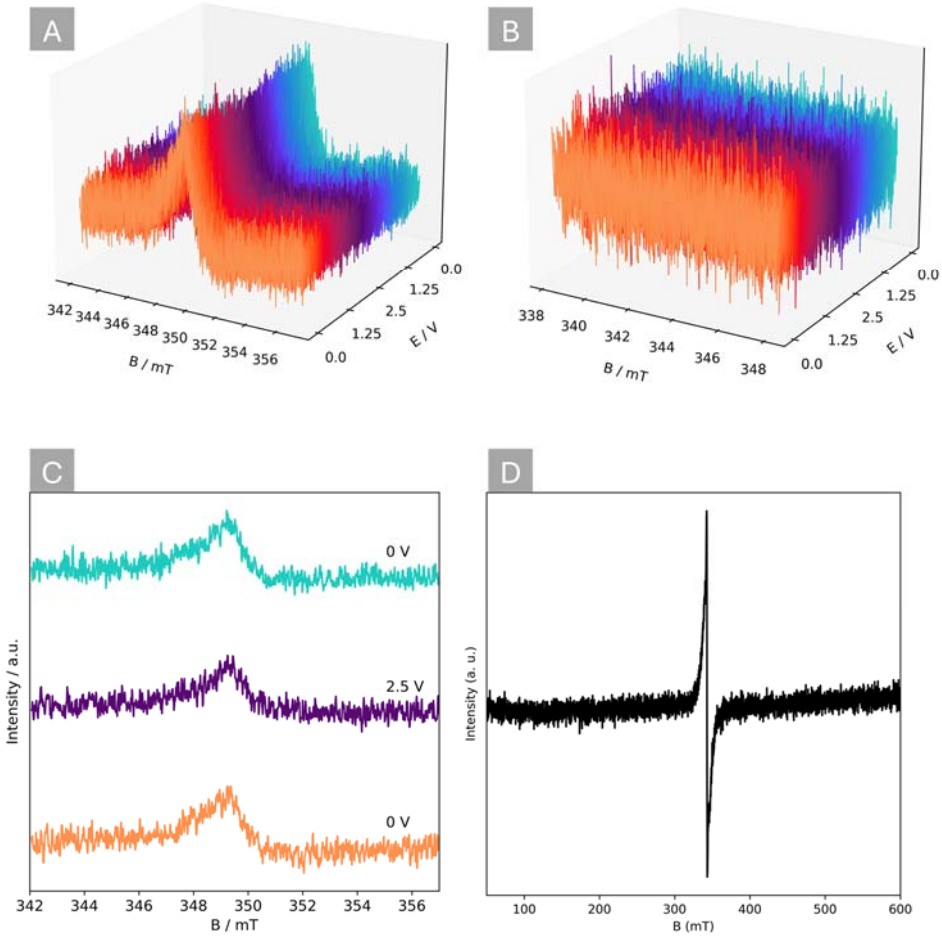

Fig. S1: *In situ* EPR measurements at 1 mW and 3 G for **(A)** pure OLC and **(B)** CMC binder. OLC exhibits a weak paramagnetic signal with a high signal-to-noise ratio and minimal changes during the measurement. In contrast, CMC binder shows no detectable paramagnetic signal, which proves its non-paramagnetic nature and therefore excludes an influence on the measurement. **(C)** Individual ESR spectra of OLC recorded at selected voltages, showing no significant differences during the charging process. **(D)** EPR spectrum of dry OLC powder displays a single signal likely associated with highly localized defects, like those observed in graphene.[S1]

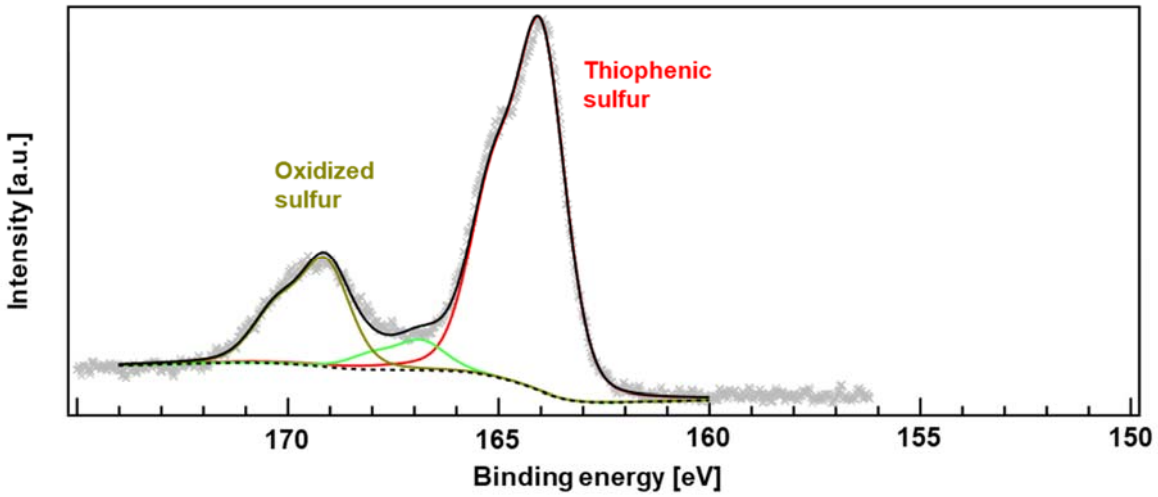

Fig. S2: XPS spectrum of the *S2p* orbital, revealing thiophenic and oxidized sulfur. The same batch of material was used in a previous work, in which a detailed XPS analysis was conducted. The figure was reused under licence *CC BY 4.0* from *ref.*[S2]

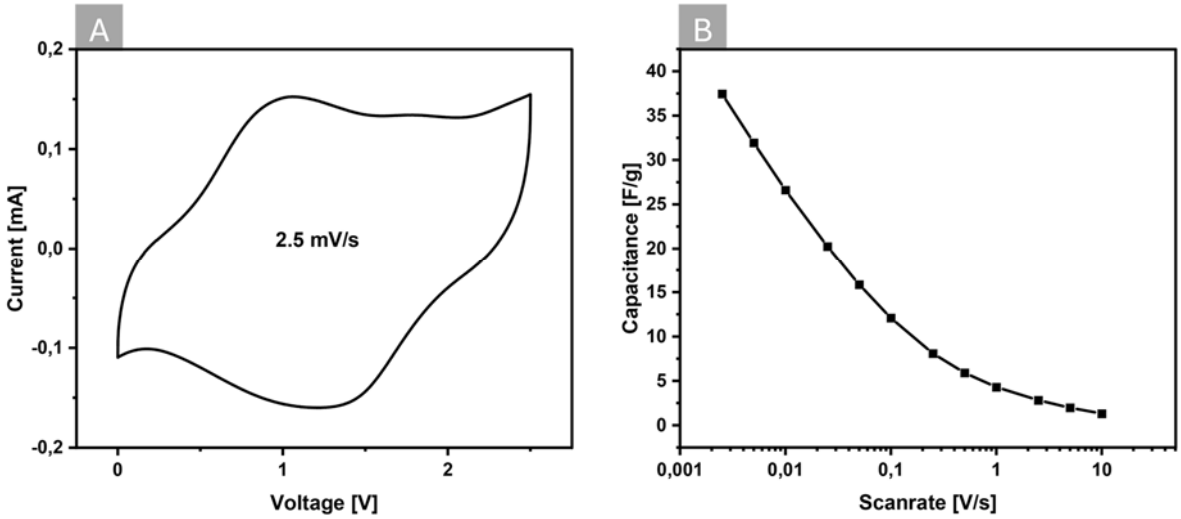

Fig. S3: Electrochemical performance of pure sulfur doped carbon: **(A)** Cyclic voltammogram at 2.5 mV/s, displaying broad redox peaks and no rectangular shape. This is indicative of a high amount pesudocapacitance. **(B)** Capacitance as a function of scan rate, showing a drastic decay: only ~10% of the initial value remains at 5 V/s.

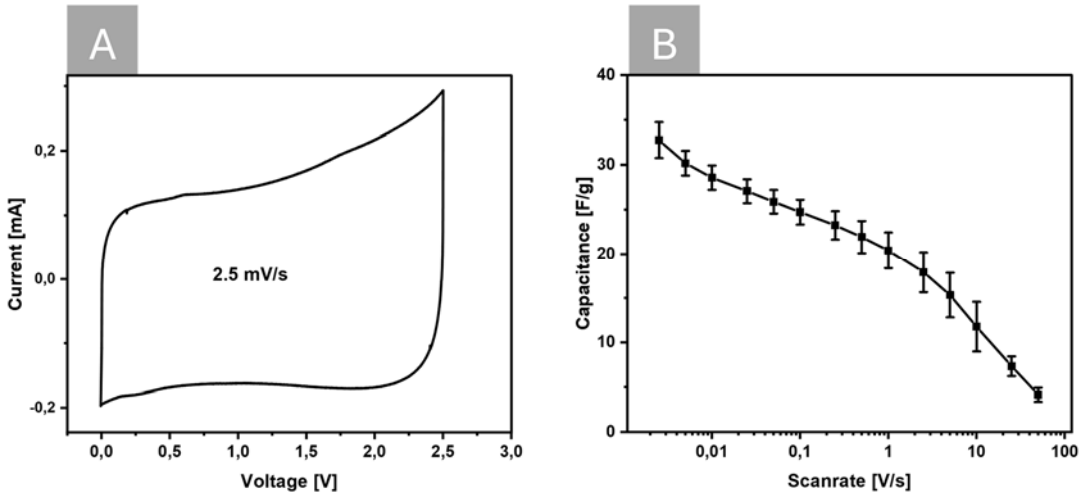

Fig. S4: Electrochemical performance of OLC: **(A)** Cyclic voltammogram at 2.5 mV/s, displaying a nearly rectangular shape without redox peaks indicative of pure supercapacitive behaviour. **(B)** Capacitance as a function of scan rate, showing high capacitance values maintained at scan rates up to 5 V/s.

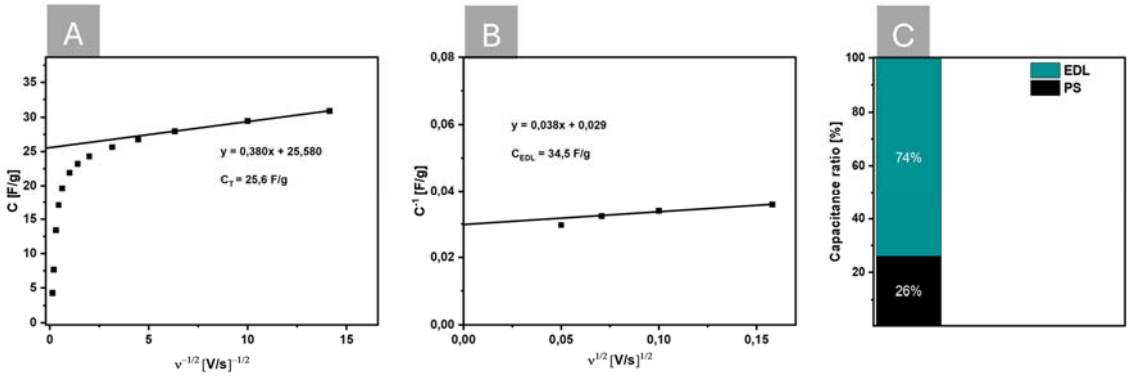

Fig. S5: Electrochemical analysis of OLC using the Trasatti method. **(A)** Trasatti plot illustrating the extrapolated total capacitance and **(B)** showing the proportion of EDL capacitance. **(C)** Ratio of pseudocapacitive to EDL charge contributions, confirming that OLC exhibits predominantly EDL behaviour with minimal pseudocapacitive contribution.

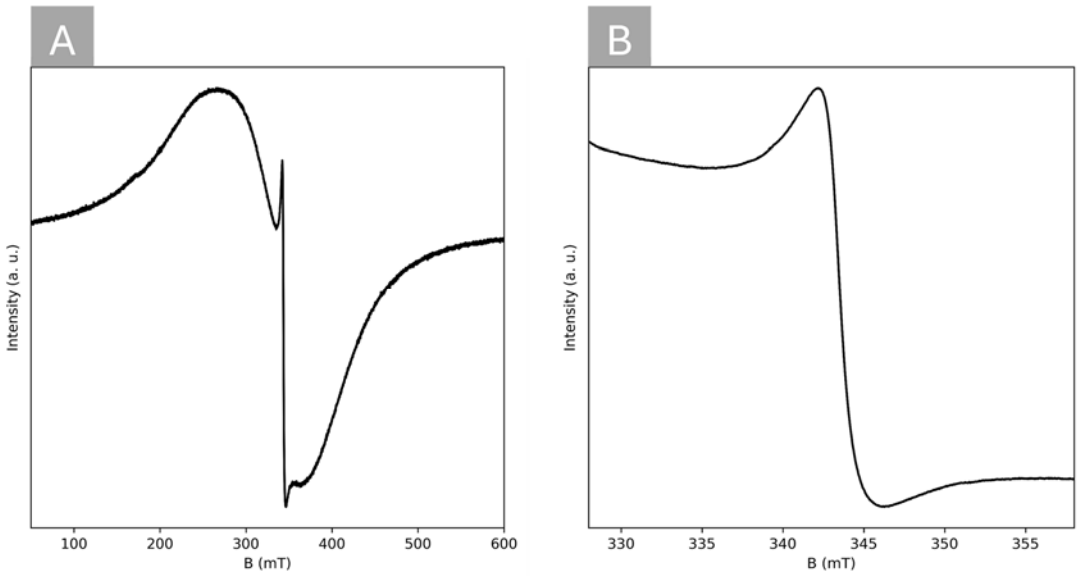

Fig. S6: Electron spin resonance analysis of sulfur-doped carbon powder after synthesis, measured at 1 mW with no voltage applied: **(A)** 3 G EPR spectrum showing high asymmetry. **(B)** Detailed scan of the g = 2 region, highlighting the spectral features of the material.

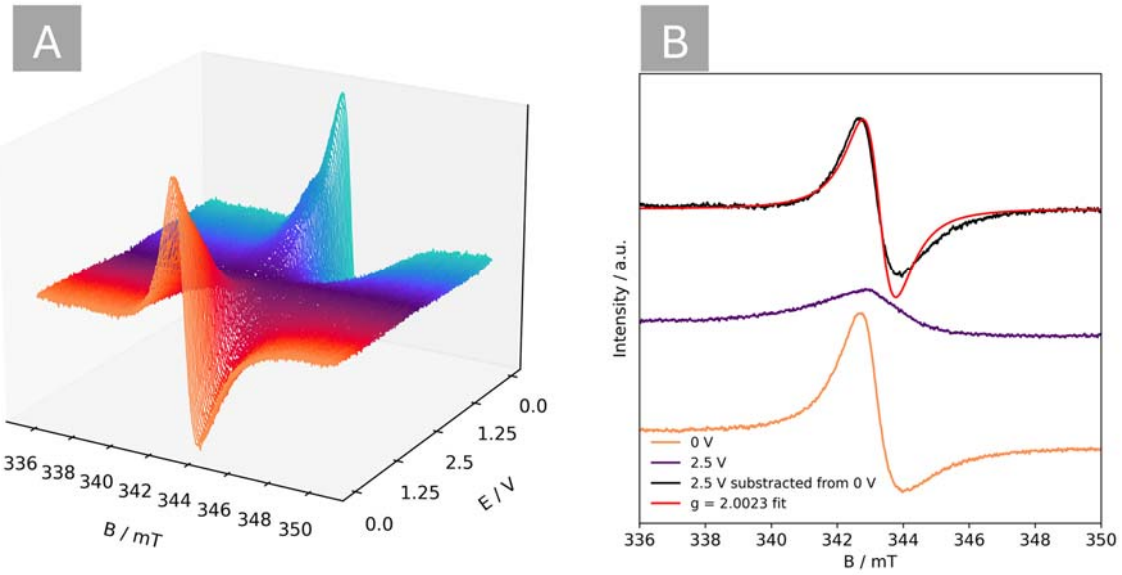

Fig. S7: **(A)** Subtraction of the purely Dysonian EPR spectrum measured at 2.5 V from all other recorded spectra displays the evolution of the voltage dependent Lorentzian signal. **(B)** Fit of the residual signal gives a g value of g = 2.0023.

References

[1] O.V. Yazyev, M.I. Katsnelson, Magnetic Correlations at Graphene Edges: Basis for Novel Spintronics Devices, Physical Review Letters 100(4) (2008) 047209. https://doi.org/10.1103/PhysRevLett.100.047209

[2] T. Neff, J. Heßdörfer, A. Bilican, L. Kolb, F. Reinert, A. Krueger, Superior Sulfur-Doped Carbon Anodes for Sodium-Ion Batteries through Incorporation of Onion-Like Carbon, Electrochimica Acta (2025) 146912. https://doi.org/10.1016/j.electacta.2025.146912