Electronic Supplementary Information

Spins at work: probing charging and discharging of organic radical batteries by electron paramagnetic resonance spectroscopy

Ilia Kulikov, \ddagger^a Naitik A. Panjwani, \ddagger^a Anatoliy A. Vereshchagin, \ddagger^b Domenik Spallek,^{*a*} Daniil A. Lukianov,^{*b*} Elena V. Alekseeva,^{*ab*} Oleg V. Levin,^{*b*} and Jan Behrends^{*a*}

^a Berlin Joint EPR Lab, Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, D-14195 Berlin, Germany

E-mail: j.behrends@fu-berlin.de

^b Electrochemistry Department, St. Petersburg State University, 7/9 Universitetskaya nab., St. Petersburg, 199034, Russian Federation

[‡] These authors contributed equally to this work.

S1 Experimental section

Quartz substrates (QSIL GmbH) were cleaned by sonicating in Acetone, rinsing in Hellmanex detergent followed by deionized water, further sonicating in Isopropyl alcohol and then rinsing with Ethanol. As a final step the substrates were placed inside a UV Ozone cleaner (Ossila, UK) for 10 minutes. The electrolyte used for all electrochemistry measurements (CV or chronoamperometry) was made using Tetraethylammonium Tetrafluoroborate as salt (Et_4NBF_4 , 99 %, Sigma Aldrich) and Acetonitrile as solvent (anhydrous, 99.8 %, Sigma Aldrich). Rinsing of all freshly prepared films was done using Acetonitrile (anhydrous, 99.8 %, Sigma Aldrich) and Propylene Carbonate (anhydrous, 99.7 %, Sigma Aldrich). Metals used for deposition of electrodes on substrates using thermal evaporation were Chromium (99.980–99.998%) and Gold (99.999%) (Kurt J. Lesker Company Ltd.). The reference electrode was a 250 μ m Silver wire (\geq 99.99 %, Sigma Aldrich).

All cwEPR spectra (except for the cwEPR spectrum in Fig. 8) were recorded at X-band frequencies (~9.4 GHz) using a laboratory-built EPR spectrometer. For all EPR spectra the magnetic field axes were rescaled to a microwave frequency of either 9.6 GHz or 9.4 GHz in order to facilitate comparability between different spectra. The magnetic field was regulated using a Bruker BH15 field controller and monitored with a Bruker ER 035M NMR Gaussmeter while a Bruker ER 041 MR microwave bridge (with a ER 048 R microwave controller) was used for microwave generation (200 mW source) and detection (diode-detection). The static magnetic field was modulated at 100 kHz and lock-in detection was carried out using a Stanford Research SR810 lock-in amplifier in combination with a Wangine WPA-120 audio amplifier. The lock-in detection leads to the derivative spectra. An ESR 910 helium flow cryostat together with an ITC503 temperature controller (Oxford Instruments, UK) was used for low-temperature measurements. *g*-factor calibration was additionally done using a N@C₆₀ powder sample at room temperature, with g = 2.00204.⁵ SEC cwEPR spectra were taken using the setup described earlier, using a on-substrate electrode setup, with a polymer film deposited on the WE using electropolymerization, and modified EPR tube where the electrolyte was 0.1 M solution of Et₄NBF₄ in ACN ($\varepsilon \approx 40$, T_{melt}=227 K). Control over the redox potential of the cell was achieved by using a Keithley 2450-EC potentiostat.

CV curves were measured either in a 5 ml beaker using the on-substrate WE, a coiled Pt CE and an Ag/AgNO₃ RE with the above mentioned electrolyte (Fig. 1c) or in a modified EPR tube for in-operando measurements (Fig. 1d), with the on-substrate WE and CE and a Ag or Ag/AgCl wire as a RE with the same electrolyte. In-operando SEC cwEPR measurements were done by holding the sample at the redox potential of interest for 200 s using the chronoamperometry mode on the Keithley 2450-EC potentiostat, while the cwEPR scans were accumulated. The 200 s scans allowed for cwEPR spectra with a suitable S/N without causing any noticeable degradation to the electrochemical cell up to a potential of 950 mV.

The potential-dependent cwEPR spectra were recorded at room temperature for in-operando measurements and at 150 K for ex-situ measurements without electrolyte. The low temperature measurements provide an increased S/N for the cwEPR spectra and therefore allowed for a better deconvolution of the spectral components contributing to the signal. The potential-dependent in-operando cwEPR spectra were measured for p-DiTS, while the ex-situ cwEPR spectra were measured for both p-DiTS and p-NiMeOSalen films.

Pulse EPR measurements (and the cwEPR measurement in Fig. 8) were carried out at X-band (9.6 GHz) using a Bruker Elexsys E 580 spectrometer equipped with a 1 kW TWT microwave amplifier (Applied System Engineering, USA) and a ER 4118X-MD5 dielectric ring resonator. Temperature control was achieved with the use of a helium flow cryostat (CF935) and an ITC5 temperature controller (Oxford instruments, UK). The echo-detected field sweep was recorded using the Hahn echo sequence of $\frac{\pi}{2} - \tau - \pi - \tau$ – echo with $\frac{\pi}{2} = 20$ ns and $\tau = 190$ ns. The intensity of the refocused Hahn echo was integrated within a 60 ns integrator gate centered at the maximum of the echo time trace which arrived at $t = 2\tau$ after the $\frac{\pi}{2}$ pulse. The pulse sequence was repeated each 1.02 ms to avoid possible saturation effects.

The spin-spin relaxation times T_2 were measured in the echo decay experiment, with a sequence depicted in the inset in Fig. 8b. A sequence of $\frac{\pi}{2} - \tau - \pi - \tau$ – echo was applied with $\frac{\pi}{2} = 20$ ns and a variable $190 < \tau < 1400$ ns. The intensity of the decaying echo was recorded as a function of the delay τ with a step of 8 ns and plotted as a function of 2τ . The integrator gate width was 60 ns. The pulse sequence with incrementing τ was repeated each 1.02 ms to avoid possible saturation effects.

S1.1 Fabrication of the modified tube

The volume of the cell used in this study had to be minimized, as the high dielectric constant of the electrolyte does not allow for the critical coupling of the resonator. The volume of the electrolyte was minimized by flattening the tip of the quartz (melting point $T_m = 1660 - 1710$ °C) tube accommodating the cell. For that, a tungsten (W, $T_m = 3420$ °C) rod of a 3.70×1.35 mm rectangular cross section, narrowing to the bottom of the tube at a wedge angle of $\alpha \approx 5^\circ$, was inserted into the tube (Fig. S1). The tube was evacuated and filled with He to a pressure of 100 mbar. The tip of the evacuated tube was molten around the thermally expanded rod with a Hydrogen-Oxygen burner ($T_f = 3080$ °C). The modified tube was then connected to atmosphere and the cooled, contracted rod was removed and later reused for modifying other tubes. The tungsten rod was fabricated from an electrode of a flash lamp of a pulsed Nd:YAG laser.



Fig. S1 Modifying the tip of the standard 5 mm OD quartz EPR sample tube by melting it around a Tungsten (W) forming rod with a H_2/O_2 burner in an evacuation setup.

The modification of the tip of the tube provided a decrease in the volume of the electrolyte down to 45 μ L, while the cylindrical part of the tube allowed for fitting the substrate connector and the wiring in. That allowed for the room temperature EPR measurements on the electrochemical cell during charging and discharging. Extensive care had to be taken to reproduce the cv curve in the modified tube as the limited volume of the electrolyte was distributed over the large surface area. That caused poor ionic transport in the electrolyte layer.

S1.2 Ag/AgCl reference electrode

The Ag/AgCl reference (RE) electrode was formed by coating a layer of AgCl onto a 250 µm Ag wire galvanically from a 1 M aqueous solution of KCl. For that, the Ag wire and a Pt wire were connected as a cathode and an anode respectively to 10 mL of the KCL solution and a DC potential of 500 mV was applied for 7500s which resulted in a dark AgCl layer deposited onto the Ag cathode. In the beginning of the galvanic deposition, the current through the KCl solution was changing in a jumpy manner, that indicated the growth of the AgCl layer. The galvanic process was stopped after the current was stable for at least 300s.

S2 Q-factors and cwEPR spectra for p-DiTS in standard and modified tube

The electrochemical cells based on the modified tube allow for higher EPR signals as compared to the normal X-band EPR tube. Fig. S2 represents two sets of measurements that describe the enhancement of the EPR signal for the modified tube. When the cell is inserted closer to the resonator's center, the Q factor of the resonator lowers and the EPR signal increases, because the intensity of the magnetic component of the microwave field B₁ is higher in the center of the resonator. When the cells were inserted closer to the center of the resonator, the Q factor went from ≈ 6000 down to $\ll 400$, so that the microwave bridge could not be critically coupled to the resonator and no EPR measurements were possible. Depending on the volume of the electrolyte in the cell, it can be inserted more or less deep into the resonator.

The modified tube could be inserted 4 mm deeper into the microwave resonator (see Fig. S2). The EPR signal in the modified tube is increased as compared to the normal tube at the same height.



Fig. S2 cwEPR signal intensity and Q factors for the standard 5 mm OD quartz EPR sample tube and for the modified tube at different heights from the center of the Bruker ER 4122-SHQE resonator. v = 9.4 GHz. Simulations of the cwEPR spectra with adjusted microwave phase. Noise analysis.



cwEPR Parameters: Attenuation 22 dB, Modulation Amplitude 0.5 mT, Modified Tube



cwEPR Parameters: Attenuation 22 dB, Modulation Amplitude 0.5 mT, 150 K, Standard Tube

Fig. S3 Sample information. Deposition CV curves, Cleaning CV curves, EPR parameters, Figure references.

S4 p-DiTS in-operando redox series

Here we present the cwEPR spectra at each measured potential during the in-operando redox series for the 8 CV cylce (t = 40 nm) p-DiTS film. We fit the experimental data with a two component fit consisting of component 1 describing the densely packed on film immobilized nitroxide spins and component 2 describing the dilute mobile nitroxide spins in electrolyte. All simulation parameters and relative weights of the two components are shown in Fig. S4.



Fig. S4 Room temperature in-operando SEC cwEPR on a 8-CV p-DiTS film. v = 9.4 GHz. black - experimental spectra, green - simulation consisting of two components with relative weight as shown in the plot, dashed-red - component 1 the coupled spins in the film, blue - component 2 the dilute mobile spins in electrolyte. All simulation done using Easyspin.¹

Fig. S5 shows the in-operando study on a 150-deposition-cycle t = 400 nm film, that has not undergone the cleaning procedure. Here we see that non-polymerized monomeric DiTS is released into electrolyte, confirmed by measuring the in-operando and used electrolyte cwEPR spectra, along with comparison to a 100 μ M sample of monomeric DiTS in solution.



Fig. S5 Top: Room temperature SEC cwEPR on 150-CV p-DiTS film. v = 9.4 GHz. This film has not undergone the cleaning/rinsing procedure and therefore as expected we see spectral signatures of the DiTS monomer which is released into the electrolyte and exhibits a five-line structure characteristic of di-tempo systems with changes in the exchange coupling associated with changes in the nitroxide – nitroxide distance. This figure shows the primary release of monomeric DiTS from a raw p-DiTS film into electrolyte (Modulation amplitude 0.1 mT – overmodulated). Bottom: cwEPR of DiTS monomer in electrolyte 100 μ M concentration at room temperature for comparison (Modulation amplitude 0.02 mT).





Fig. S6 Room-temperature in-operando cwEPR measurements for two p-DiTS electrochemical cells. v = 9.4 GHz. Two-component spectral deconvolution to identify dilute and packed nitroxide fragments. Spectrum of the rest electrolyte. a): Cell with a p-DiTS film grown by 150 deposition cycles ($t \approx 400$ nm) that was left untreated and underwent one charge-discharge cycle before the measurement. The dilute component is released during the oxidation and remains detectable in the rest electrolyte. b): Cell with a p-DiTS film grown by 200 deposition cycles ($t \approx 500$ nm) that was rinsed in solvents and cycled in the electrolyte to remove the not polymerized nitroxide fragments. The initially released dilute component is electrochemically active and does not appear in the rest electrolyte.



Fig. S7 a): Evolution and component decomposition of cwEPR spectra for a tube-based, 150 CV p-DiTS ORB upon 36 charge-discharge cycles. b): Quantitative analysis of the separated spectral components. v = 9.4 GHz, Mod. Amp: 0.5mT. Quantitative analysis of the CV curves. c): Cyclic voltammograms of the cell, recorded with respect to Ag/AgCl RE at a rate of 5 mV s⁻¹ in between the EPR scans, in the modified tube inside the microwave resonator. The CV were taken at 5 mV s⁻¹, which is 10 times slower than the CV curves taken in the larger beaker, because limited amount of the electrolyte in the modified tube was found to strongly affect the shape and positions of the CV peaks at higher speeds of cycling.

The degradation of p-DiTS cells was monitored simultaneously by cwEPR and cyclic voltammetry. The number of paramagnetic species in the cells was changing during the degradation cycling. That change was quantified from both EPR and electro-chemistry perspective. Quantitative analysis of the simulated components comprising the cwEPR spectra was done with the Spincounting Toolbox² (developed by Christopher Engelhard) in Matlab. Cells with the electrolyte

exhibit weaker signals as compared to the dry films, so an intensity scaling factor was determined and taken into account.

The CV curves during the degradation of the cells were quantitatevly analyzed. The reduction branches were integrated versus time to obtain the charge transferred to the film at each degradation cycle. The integrals are shown in S10. The total transferred charge during the reduction of the film is a three-electron process,³ where two electrons are transferred to the TEMPO groups and one electron is transferred to the backbone. Therefore, the number of electrons transferred to TEMPO is 2/3 of the total charge transferred to the film divided by the elementary charge. With that, the number of electro-chemically active TEMPO groups was determined at each degradation cycle.

We observed two pathways of the degradation of p-DiTS: the release of paramagnetic nitroxide fragments and the overall decrease in the cwEPR signal after a charge-discharge cycle, that is connected to the formation of diamagnetic, or oxidized, electrically isolated domains within the film. The latter may, possibly, be accompanied by a release of the diamagnetic fragments to the electrolyte.

While the cell in S6 a almost fully recovers its initial signal intensity, the cell in Fig. S6 b loses 51% of its initial spin count after being reduced back to its paramagnetic state (from 8.0E+15 spins to 3.7E+15 spins, cf. Fig. S6, bottom subplots for the spin count data). That indicates, some fragments have lost electrical connection to the rest of the film, and stayed in an oxidized, diamagnetic state. The dramatic decrease in spin count can be accounted for by the disappearing "dilute" component only partially, as the dilute component yields maximum 2.7E+14 spins (at 600 mV) which is only 3% of the total spin count. The remaining 48% of missing spins can not be explained by the release of paramagnetic fragments. We propose that some fragments of the film are losing connection to the electrode during the oxidation process. These EPR silent, oxidized nitroxide fragments may stay in the film or may leave it. That process is observed only indirectly as a change of the overall EPR signal intensity, when the cell undergoes a full charge-discharge cycle.



Fig. S8 Ex-situ SEC cwEPR measurements (ν =9.4 GHz) on a dry p-DiTS film at 150 K. Decomposition of spectra into two components with numeric simulations using EasySpin¹: a broad Lorentzian line (g = 2.0070, lw = 4.63±1.00 mT) and a dilute component with a hyperfine coupling to ¹⁴N (I = 1, g = [2.00231 2.00711 2.00912], A = [100 15 15]±5 2 2]MHz, Lorentzian broadening with lw = 1.65 mT). The absorption profiles are shown with the integrals of the EPR signals. The ratio between the simulated components for each potential is shown by the double integrals of the components. Inset: sum of the broad and dilute components that reproduce the line shape at 0.6V.



Fig. S9 Ex-situ SEC cwEPR measurements (ν =9.4 GHz) on a dry p-NiMeOSalen film at 150K. Decomposition of spectral lines into three components with numeric simulations using EasySpin.¹ Three components are based on Ref. 4 and correspond to signals 1, 2' and 2. Relative intensities of the doubly integrated signal components at various potentials.

We investigated p-NiMeOSalen using ex-situ SEC cwEPR where the exact potentials of the film may have equilibrated to potentials slightly away from the set potentials. However, the increased S/N achieved by low-temperature measurements allow us to better resolve spectral features.

The ex-situ SEC cwEPR of p-NiMeOSalen at 150 K at a few key potentials is shown in Fig. 7b, while the full data set is shown in Fig. S9. At 0 V (vs. Ag/AgNO₃) we observe an EPR signature which is consistent with what was denoted signal 1 in Ref. 4, where we obtain an S = 1/2 cwEPR spectrum which can be simulated using a *g*-tensor with principle values of [1.9984, 2.0094, 2.0235], consistent with those determined by Dmitrieva *et al.*, cf. [1.9990, 2.0094, 2.0240]. Signal 1 can be attributed to a phenoxyl radical, based on the *g*-tensor being closer to an organic radical rather than a nickel (III) centered spin where the *g*-factor (g_{iso}) is usually around 2.12–2.18.^{6,7}

Dmitrieva *et al.* also observed a change in the EPR signal as a function of oxidation potential, towards signals which are described by an isotropic *g*-factor of 2.0084 and 2.0067, denoted signal 2' and 2 respectively. In our ex-situ measurements we observe contributions from more than one of the above mentioned signals at each potential. As we increase the oxidation potential, we see a significant change in the spectrum with decreasing structure. The p-NiMeOSalen signals were deconvoluted into a weighted sum of the three spectral components described as signal 1, 2' and 2 in Ref. 4. Overall we observe that at 0 V we have a major contribution from signal 1 and a minor contribution from signal 2'. Increasing the potential leads to increasing contributions from either signal 2' or 2 depending on the potential, and by 1.3 V we see only contributions from signal 1 and 2' again, however the overall signal intensity is decreased, as expected for a signal attributed to the formation of diamagnetically coupled bi-polarons. However, since our measurements are ex-situ and because CV cycling leads to trapped charges (non-reduced fragments due to inaccessibility), we do not see clear transitions from signal 1 to signal 2' and 2.

Based on the p-DiTS and p-NiMeOSalen ex-situ studies it is clear that both the TEMPO and NiSalen backbone are redox active, as expected. Therefore, the absence of a clear NiSalen signal in p-DiTS is surprising. The film thicknesses for p-DiTS and p-NiMeOSalen used in the ex-situ studies differ by a factor of 2. Hence, we should still expect to see the NiSalen signal in the p-DiTS measurement at increasing oxidation potentials where the TEMPO signal has decreased. Further work on understanding the behavior of the electron transfer mechanism from the nitroxide groups to the backbone structure is ongoing.





Fig. S10 Degradation of capacity of a p-DiTS film upon 36 charge-discharge cycles. Transferred charge calculated as integrals of the reduction branches of the CV curves. By the last charge-discharge cycle the film can accept 10 times less the charge as in the beginning of the cycling.

Supplementary References

- 1 S. Stoll, A. Schweiger, Journal of Magnetic Resonance, 2006, 178, 42.
- 2 Spincounting Toolbox for Matlab developed by Christopher Engelhard, https://github.com/lcts/spincounting
- 3 A. A. Vereshchagin, D. A. Lukyanov, I. R. Kulikov, N. A. Panjwani, E. A. Alekseeva, J. Behrends, O. V. Levin, *Batteries & Supercaps*, 2021, 4, 336.
- 4 E. Dmitrieva, M. Rosenkranz, J. S. Danilova, E. A. Smirnova, M. P. Karushev, I. A. Chepurnaya, A. M. Timonov, *Electrochimica Acta*, 2018, **283**, 1742.
- 5 J. J. Wittmann, T. V. Can, M. Eckardt, W. Harneit, R. G. Griffin, B. Corzilius, J. Magn. Reson., 2018, 290, 12.
- 6 F. Thomas, Dalton Trans., 2016, 45, 10866.
- 7 O. Rotthaus, O. Jarjayes, F. Thomas, C. Philouze, C. P. D. Valle, E. Saint-Aman and J.-L. Pierre, *Chem, Eur. J.*, 2006, 12, 2293.