

Probing Charging and Discharging of Organic Radical Batteries by EPR

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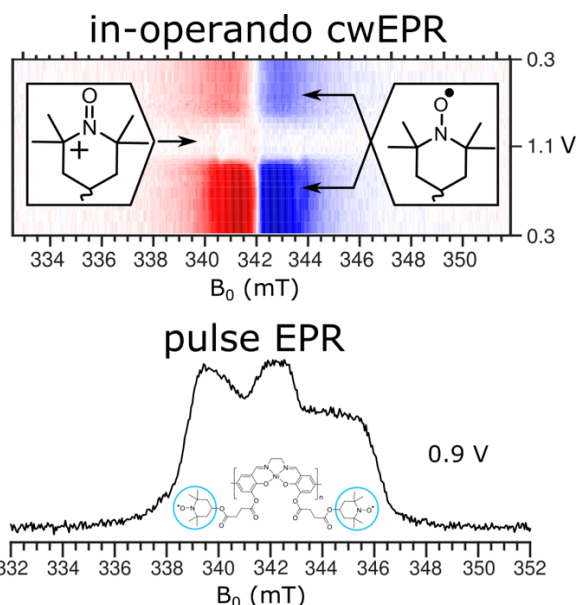
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Electron spins are unique local probes for elucidating redox reactions associated with the operation of organic radical batteries (ORBs). EPR spectroscopy can thus be employed to study charging and discharging processes in this promising class of electrochemical power sources based on organic radicals as redox-active groups.

Here we report on the development of a versatile on-substrate electrode setup for spectroelectrochemical EPR measurements on redox conductive polymers for ORBs [1]. Quantitative in-operando EPR experiments performed on electrochemical cells with a di-TEMPO Ni-Salen polymer as active electrode material demonstrate a strong decrease in the number of paramagnetic centres upon oxidising the film [2]. The distinct EPR signatures of the TEMPO-containing polymer and its fragments in different molecular environments are used to study its degradation upon repeated cycling. A comparison between the number of EPR-active sites and the number of electrochemically active charges, as measured by cyclic voltammetry, provides information on the nature of the degradation process.

Low-temperature ex-situ pulse EPR measurements on the oxidised polymer film reveal the spectrum of dilute nitroxide species, which may be associated with electrochemically inactive islands. These experiments pave the way for advanced EPR techniques for accurately determining distances between adjacent paramagnetic centres and thus for identifying performance-limiting loss mechanisms, which can eventually help develop strategies for making ORBs powerful contenders on the path towards sustainable electrochemical power sources.



References

- [1] I. Kulikov, N. A. Panjwani, A. A. Vereshchagin, D. Spallek, D. A. Lukianov, E. A. Alekseeva, O. V. Levin, J. Behrends, *ChemRxiv*, DOI: 10.26434/chemrxiv-2022-zctv6 (2022)
- [2] A. A. Vereshchagin, D. A. Lukyanov, I. R. Kulikov, N. A. Panjwani, E. A. Alekseeva, J. Behrends, O. V. Levin, *Batteries & Supercaps* **4**, 336 (2021)