

EPR-ON-A-CHIP FOR *OPERANDO* MONITORING OF PARAMAGNETIC SPECIES IN SOLUTION

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EPR-on-a-Chip (EPRoC) technology integrates microwave excitation and EPR detection into the coil of a single voltage-controlled oscillator on a microchip. Its wide frequency tunability enables the use of permanent magnets, drastically reducing spectrometer size and cost [1]. Coated with a protective parylene layer, the chip functions as a submersible dipstick sensor for direct immersion in sample solutions.

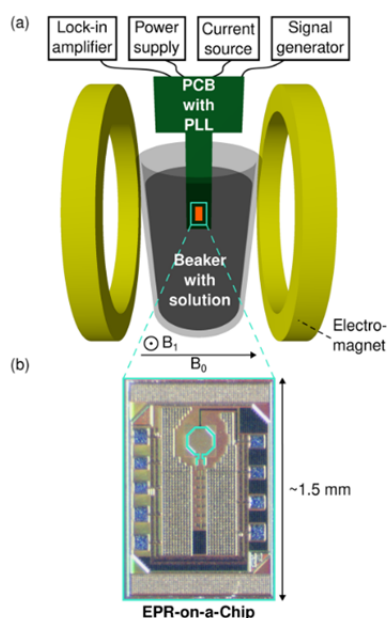


Figure 1 EPRoC dipstick configuration with the chip submerged in solution. (b) Close-up of the EPRoC sensor showing the octagonal VCO coil of approx. 200 μm diameter serving as the sensor. Figure adapted from [2].

We present several *operando* applications of this platform. Quantitative tracking of VO^{2+} in vanadium redox flow battery electrolytes yielded state-of-charge values in good agreement with commercial X-band EPR [2]. Rapid scan EPRoC [3] enabled real-time monitoring of dissolved oxygen concentration via trityl radical linewidth broadening [4]. Additionally, we demonstrate *operando* spectro-electrochemistry by detecting semiquinone radical intermediates during benzoquinone redox reactions directly at the electrode. To overcome the limited sensing volume inherent to on-chip coils, we have developed inductively coupled resonators that increase the active volume and enable detection through intervening

materials, allowing remote sensing in harsh environments inaccessible to the chip itself.

These results establish EPRoC as a versatile, miniaturized platform for *in situ* EPR monitoring of coordination compounds and radical processes.

- [1] M. Kern, A. Chu, and J. Anders, 'Current Trends in VCO-Based EPR', *Appl Magn Reson*, vol. 55, no. 9, pp. 1065–1089, Sep. 2024, doi: 10.1007/s00723-024-01698-0.
- [2] S. Künstner *et al.*, 'Monitoring the state of charge of vanadium redox flow batteries with an EPR-on-a-Chip dipstick sensor', *Phys. Chem. Chem. Phys.*, vol. 26, no. 25, pp. 17785–17795, Jun. 2024, doi: 10.1039/D4CP00373J.
- [3] S. Künstner *et al.*, 'Rapid-scan electron paramagnetic resonance using an EPR-on-a-Chip sensor', *Magnetic Resonance*, vol. 2, no. 2, pp. 673–687, 2021, doi: 10.5194/mr-2-673-2021.
- [4] J. E. McPeak *et al.*, 'Operando detection of dissolved oxygen in fluid solution using a submersible rapid scan EPR on a chip dipstick sensor', *Sci Rep*, vol. 15, no. 1, p. 9872, Mar. 2025, doi: 10.1038/s41598-025-93591-4.