Application Note

Scanning Electrochemical Microscopy (SECM) for ORR selectivity evaluation of Pt-free catalysts

Application Note: 2024

Fuel cells have long been valued for their environmental benefits, offering a clean energy conversion method free from harmful greenhouse gases. Despite their advantages, the development of fuel cells has been hindered by high costs, particularly due to the expensive cathode electrocatalysts required for the oxygen reduction reaction (ORR). To evaluate catalytic activity before advancing to membrane electrode assembly (MEA) testing, methods like the rotation disk electrode (RDE) and rotation ring disk electrode (RRDE) are commonly used.

However, RDE/RRDE tests often involve thicker catalyst layers to compensate for the lower intrinsic activity of Pt-free catalysts, which can obscure the true electrochemical response. Previous research has shown that RRDE results can significantly overestimate ORR performance compared to MEA results.[1]

Scanning Electrochemical Microscopy (SECM) offers a promising alternative for analyzing catalysts.[2-3] It not only maps localized current distribution but also assesses ORR selectivity by detecting peroxide. Recent work by Ndrina Limani, Renaud Cornut, and colleagues at Université Paris-Saclay has demonstrated SECM's potential by studying ultra-low loadings of a Fe-N-MWCNT catalyst. This research provided new insights into the catalyst's selectivity, revealing it to be significantly lower than what RRDE tests typically suggest, published as "Low loading ORR selectivity evaluation of Pt-free catalysts with scanning electrochemical microscopy." *Electrochemistry Communications*, **2023**, 153, 107538, https://doi.org/10.1016/j.elecom.2023.107538.[4]

The SECM experiments were originally performed with a novel two-step approach: ORR detection in Redox Competition (RC) mode and H_2O_2 detection oxidation in Substrate Generation/Tip Collection (SG/TC) mode, as shown in Fig. 1. The probe-to-substrate distance remained at 30 µm, which was achieved via the negative feedback approach.

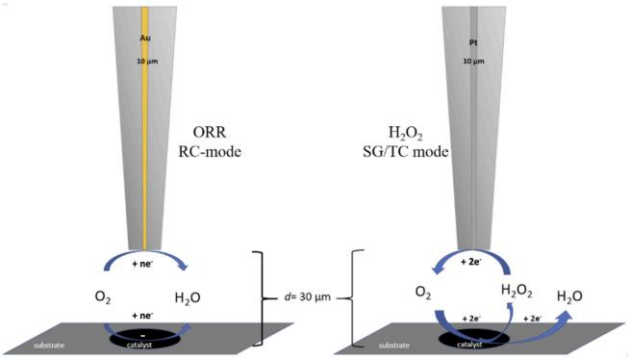


Figure 1. Schematics of the dual-electrode SECM approach. Reproduced from Ref. [4] by permission of HAL.

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During the measurements, the ORR detection step was carried out at − 0.65 V *vs.* SCE at the SECM probe, while the substrate was scanned from 0.4 V to -0.3 V *vs.* SCE at a slow scan rate of 2 mV/s to establish steady-state conditions. For peroxide detection, the substrate was again swept across the same potential range used for ORR. Concurrently, chronoamperometry (CA) was performed at 1.1 V *vs.* SCE at the SECM probe to record the oxidation of H_2O_2.

The currents obtained from the SECM probes in both experiments were utilized to calculate ***n*** using Eq. (1), like the calculation of ***n*** in RRDE experiments. However, the currents were normalized by subtracting the current value at the on-site potential of ORR from the current at all other potentials.

$$\boldsymbol{n} = 4 \times \frac{\Delta i_{O_2}}{\left(\frac{\Delta i_{H_2O_2}}{N}\right)+\Delta i_{O_2}} \qquad (1)$$

The Fe-N-MWCNT catalyst was initially studied at different electrode loadings using RRDE. The detected peroxide percentage ranged from as low as 3% at the highest loading to approximately 32% at the lowest loading. Meanwhile, the value of ***n*** varied from about 3.42 to 3.95 at ~0.63 V *vs.* RHE, as shown in Fig. 2. This trend indicates that lower-loaded deposits exhibit higher peroxide detection, consistent with previous observations from carbon-based catalysts. However, the reduced peroxide detection at higher loadings could be due to the longer diffusion path of H_2O_2 in thicker layers, potentially leading to its further reduction to H_2O within the layer before release. Additionally, peroxide disproportionation to O_2 and H_2O within the layer is also possible, complicating the determination of the catalyst's intrinsic ***n***.

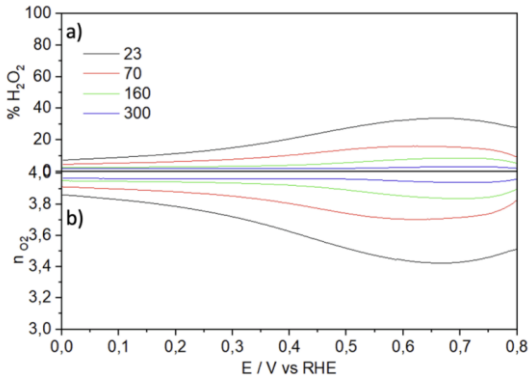


Figure 2. a) Peroxide percentage detected at the Pt ring *vs.* the potential applied at the disc for different loadings (µg/cm^2), b) the corresponding ***n*** values. Reproduced from Ref. [4] by permission of HAL.

The limitations of RRDE have been addressed by utilizing SECM as a microscale technique, allowing for the analysis of lower catalyst loadings. As depicted in Fig. 3(a), the selectivity or the number of electrons transferred towards peroxide was determined using the SG/TC mode. In this mode, the detected H_2O_2 decreases at more cathodic potentials due to a higher rate of oxygen reduction at the catalyst, resulting in a higher current at the SECM probe. Less peroxide was detected at the highest loading (0.15 nA), while a larger H_2O_2 current (1.25 nA) was observed at the lowest loading. Using background-corrected currents for ORR and H_2O_2, ***n*** was determined for all loadings, as shown in Fig. 3(b). Most curves show ***n*** as relatively independent of potential over a wide range (0 to ~0.5 V *vs.* RHE), except for the 5.7 µg/cm^2 deposit, which exhibited less stable behavior. As suggested by the trend in H_2O_2 currents, the number of electrons

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increased with loading. At 0 V *vs.* RHE, the most loaded deposit (38.4 µg/cm^2) exhibited an ***n*** of approximately 3.9, followed by the 13.8 µg/cm^2 with ***n*** ~ 3.8, the 5.7 µg/cm^2 deposit with ***n*** ~ 3.3, and finally, the 1.2 µg/cm^2 deposit with an ***n*** of only 2.6, which suggests that at lower loadings, the catalyst undergoes ORR via a pathway close to 2 electrons, in contrast to the higher loadings, which indicate a pathway closer to 4 electrons.

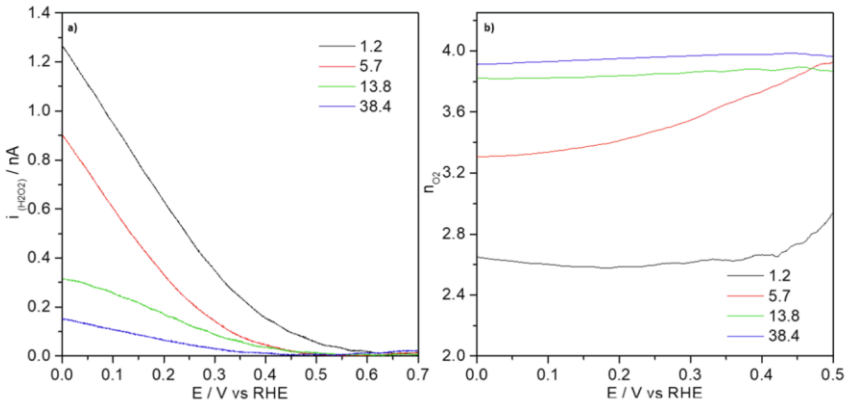


Figure 3. a) Net background corrected H_2O_2 currents, b) number of transferred electrons calculated from the ORR and H_2O_2 currents while considering N = 100%. Reproduced from Ref. [4] by permission of HAL.

This study examined the ORR selectivity and agglomerate scale of a Fe-NMWCNT catalyst using both RRDE and SECM. While RRDE measurements indicated a minimum electron transfer number of 3.2, SECM measurements at a 1.2 µg/cm^2 loading revealed a lower ***n*** value of just 2.6. This suggests that more peroxide is produced in the sample than RRDE measurements alone would indicate, especially when focusing on higher loadings where this information could be overlooked. In other words, the intrinsic selectivity of this catalyst appears to lean more towards a 2-electron pathway. This finding is particularly important for fuel cell integration, as a high peroxide yield can lead to catalyst degradation. Studying ultra-low loadings with SECM is valuable because it allows for a closer approximation of the intrinsic electron transfer number. If little or no peroxide is detected at such low loadings, it assures that the catalyst is indeed selective for ORR.

AMETEK offers the VersaSCAN scanning electrochemical system, providing spatial resolution to both electrochemical and materials-based measurements, including the SECM with RC mode and SG/TC mode. The PARSTAT 3000A-DX Bipotentiostat features hardware synchronization, providing the best coordination for RRDE experiments for Fuel Cell Catalyst evaluation.

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Reference

[1] J. Fan, M. Chen, Z. Zhao, Z. Zhang, S. Ye, S. Xu, H. Wang, H. Li, Bridging the gap between highly active oxygen reduction reaction catalysts and effective catalyst layers for proton exchange membrane fuel cells, *Nat. Energy,* **2021,** 6, 475–486.

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[4] N. Limani, A. Boudet, E. Scorsone, V. Derycke, B. Jousselme, R. Cornut, Low loading ORR selectivity evaluation of Pt-free catalysts with scanning electrochemical microscopy. *Electrochem. Commun*., **2023**, 153, 107538.

Summary – This application note illustrated the application of SECM for the intrinsic ***n*** of Pt-free ORR catalysts, especially at low loading. More peroxide production from the sample was revealed by SECM than RRDE measurements alone.

AMETEK offers the VersaSCAN scanning electrochemical system, providing spatial resolution to both electrochemical and materials-based measurements, including the SECM with RC mode and SG/TC mode, and the PARSTAT 3000A-DX Bipotentiostat with hardware synchronization, providing the best coordination for RRDE experiments for Fuel Cell Catalyst evaluation.

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