Supporting information

Benchmarking high surface area electrocatalysts in a gas diffusion electrode: measurement of oxygen reduction activities under realistic conditions

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Preparation of Nafion membrane.

Circular pieces (φ = 20 mm) of a Nafion membrane were punched from a larger sheet. The punched membranes were treated in 5 wt. % H_2O_2 aqueous solution at 80 °C for 30 minutes. Subsequently the membranes were treated in 8 wt. % H_2SO_4 aqueous solution at 80 °C for 30 minutes. Finally, the membranes were boiled in DI water at 80 °C for 30 minutes. Between each treatment the membranes were rinsed with DI water at least 3 times.

Experimental setup for the GDE cell at elevated temperature.

For measurements at elevated temperature, the GDE setup, including the gas humidifier, was placed in an aluminum box, and heated as whole by placing onto a heating plate with thermocouple control (Figure S1). The temperature inside the aluminum box was monitored and controlled by a feedback system of the heating plate. To avoid direct heating of the GDE cell and the gas humidifier

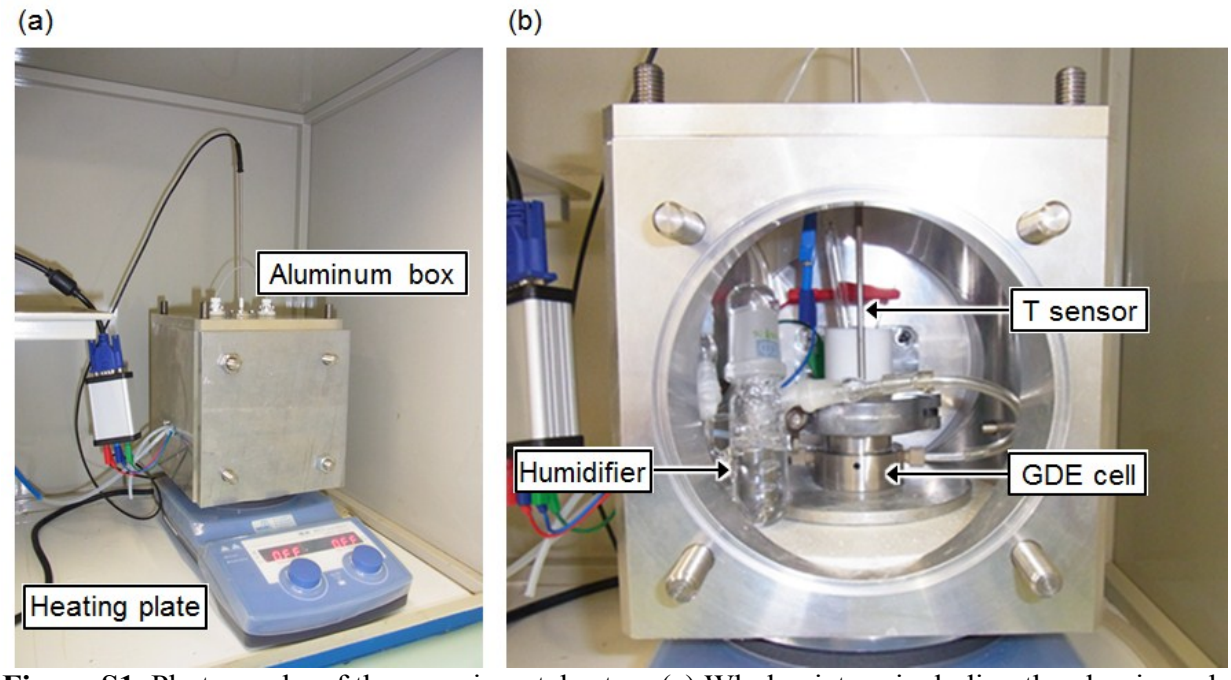

Figure S1. Photographs of the experimental setup. (a) Whole picture including the aluminum box, a temperature sensor, and a heating plate. (b) Inside of the aluminum box: The GDE cell, the gas humidifier, and the temperature sensor are placed.

a plate made of styrene foam was placed on the bottom of the aluminum box. The gas tubes and the electric wires of the potentiostat were inserted from the side slit of the aluminum box.

Using this setup, the gas introduced into the GDE cell was always fully humidified (100 %RH) at any temperature. For the measurements under non-humidified condition, the gas humidifier was removed, and the gas tube was directly connected to the GDE cell.

Catalyst layer application using a nebulizer.

The catalyst ink was sprayed on the GDL (MPL coated side) using a nebulizer (TR-30-K1, Meinhard) with Ar gas (ca. 700 ccm). During the spraying the GDL was heated on a heating plate (150 °C) and covered with a paper mask so that a circular catalyst layer (φ = 3 mm) was formed at the center of the GDL (Figure S2a). The microphotographs of the catalyst layer fabricated by drop cast method and that fabricated by spraying are shown in Figure S2b and c. With the drop cast method, a circular catalyst layer which is roughly 3 mm in diameter could be fabricated by adjusting the volume of the catalyst ink pipetted on the GDL. However, controlling the exact diameter of the catalyst layer was difficult. Furthermore, the thickness of the catalyst layer was not homogeneous and so-called coffee rings were formed. In contrast, homogeneous catalyst layers with well-defined diameter were obtained by employing the spraying method. A homogeneous catalyst layer fabricated by the spray coating method always showed improved ORR performance compared to an inhomogeneous catalyst layer fabricated by the drop cast method. This observation matches the experience of the thin film RDE technique. Representative ORR polarization curves obtained from catalyst layers fabricated by the two different methods are compared in Figure S2.

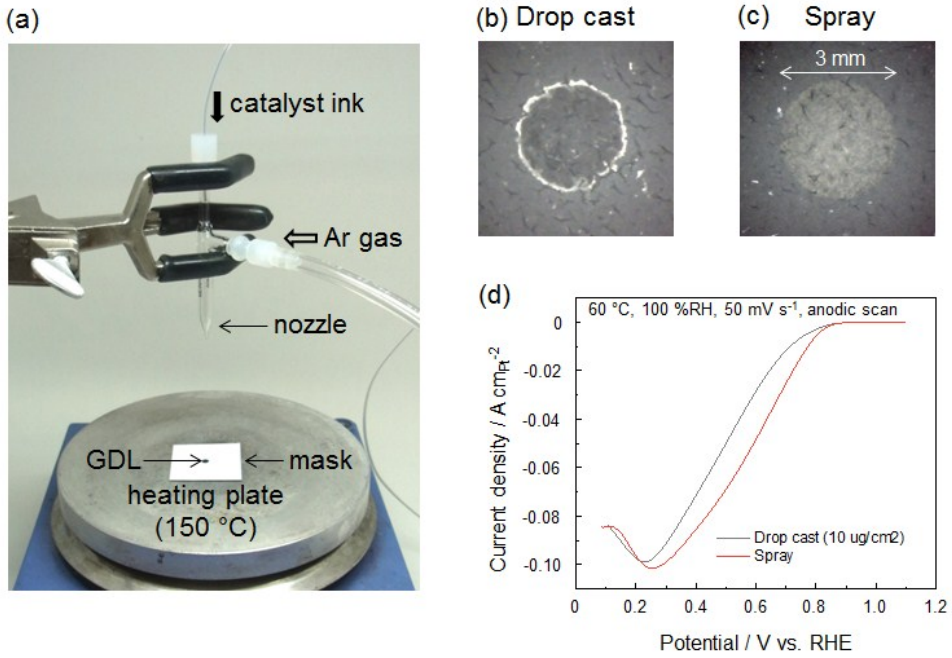

Figure S2. (a) Photograph of the experimental setup for the spray coating of the catalyst ink using a nebulizer. (b, c) Microphotographs of the catalyst layers fabricated on GDLs by the drop cast and the spray coating. (d) Comparison of the ORR polarization curves: the catalyst layer fabricated by the drop cast (gray) and the catalyst layer fabricated by the spray coating (red). The current density is normalized by RF. Both polarization curves were measured at 60 °C, 100 %RH, and scan rate of 50 mV s^{-1} (anodic).

Influence of conditioning before the measurement.

In the RDE method, catalyst samples are usually cleaned by potential cycling (up to 1.2 V vs. RHE) in Ar-purged liquid electrolytes before the measurement. In contrast, pre-conditioning steps for MEAs are more complex and sometimes they are performed in O_2 or air-purged atmosphere accompanying the oxygen reduction reaction. In the case of the GDE cell, the catalyst layer samples showed MEA-like behavior in the conditioning step: potential cycling in Ar-purged atmosphere was insufficient and potential cycling in O_2 was essential to accomplish proper pre-conditioning. It is also very important to perform pre-conditioning with IR compensation below 1 Ω as the correct potential especially at the high currents is applied to clean the electrode. In Figure S3, the ORR polarization curve measured after potential cycling in Ar (0.06-1.2 V_{RHE}, 500 mV s^{-1}, 50 cycles) and the ORR polarization curve measured after additional potential cycling in O_2 (0.06-1.1 V_{RHE}, 50

mV s^{-1}, 10 cycles) are shown. It was observed that even after the potential cycling in Ar-purged atmosphere the ORR performance significantly improved by the additional potential cycling in O_2-purged atmosphere. It is assumed that water generated by the ORR during the potential cycling facilitates the cleaning of the catalyst surface and washes away the contaminants.

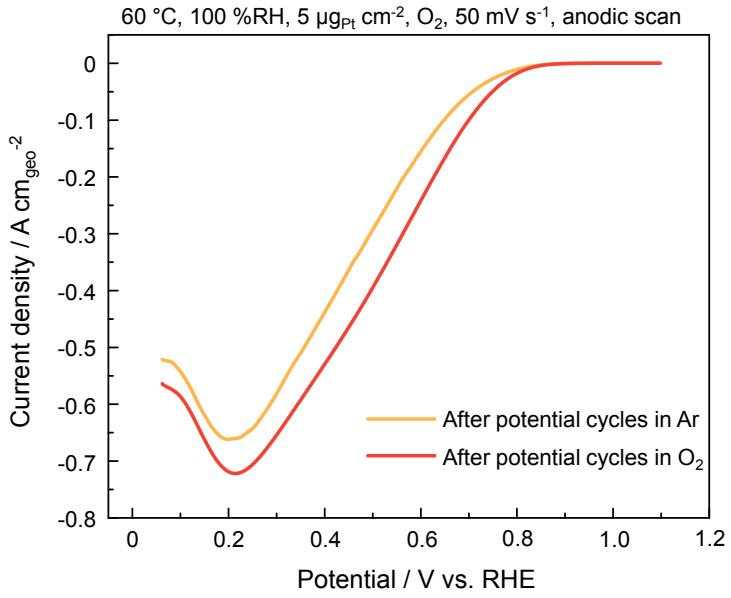

Figure S3. Impact of the conditioning: The ORR polarization curve measured after potential cycling in Ar (0.06-1.2 V_{RHE}, 500 mV s^{-1}, 50 cycles) and the ORR polarization curve measured after potential cycling in O_2 (0.06-1.1 V_{RHE}, 50 mV s^{-1}, 10 cycles) in addition to the potential cycling in Ar. The polarization curves were measured at 60 °C, 100 %RH, and scan rate of 50 mV s^{-1} (anodic).

[1] A. Zana, G.K.H. Wiberg, Y.-J. Deng, T. Østergaard, J. Rossmeisl, M. Arenz, Accessing the Inaccessible: Analyzing the Oxygen Reduction Reaction in the Diffusion Limit, ACS Applied Materials & Interfaces, (2017).