Oxygen reduction reactivity of precisely controlled nano-structured model catalysts


S1 $\mathrm{N}_{2}$ adsorption - desorption isotherms of CAG at 77 K .





S2 Obtained pore distributions using BJH method from $\mathrm{N}_{2}$ adsorption isotherm of CAG support (R/C $=100$, before deposition) ( $\bullet$ ) and RC 100 (after platinum deposition) (■) (upper graph), and $\mathrm{N}_{2}$ adsorption - desorption isotherms at 77 K (lower graph).



S3 XRD patterns of $\mathrm{Pt} / \mathrm{CAG}$ catalysts and $\mathrm{Pt} / \mathrm{CB}$. The measurements were performed using $\mathrm{CuK} \alpha$ radiation.


S4 Change in electrochemical surface area of RC 100 without any ionomers.

Cyclic voltammograms of thin film electrode of RC 100 without any ionomer under Ar saturated 0.1 $\mathrm{mol} \mathrm{dm}{ }^{-3} \mathrm{HClO}_{4}$ solution at room temperature. The amount of platinum on the electrodes was $2.8 \mu \mathrm{~g}$ (14 $\mu \mathrm{g} \mathrm{cm}^{-2}$ ). The sweep rate was $50 \mathrm{mV} \mathrm{s}^{-1}$. The electrochemical surface areas slightly changed, and were 36.8 (initial: before RDE measurement), 35.7 ( $1^{\text {st }}$ run: after $1^{\text {st }} \mathrm{RDE}$ measurement), and $35.2 \mathrm{~m}^{2} / \mathrm{g}$ ( $2^{\text {nd }}$ run: after $2^{\text {nd }}$ RDE measurement). The ECSAs decreased a few percent after the measurement (RDE), i.e., $3.0 \%\left(1^{\text {st }}\right.$ run) and $4.3 \%\left(2^{\text {nd }}\right.$ run) less from the initial surface area, and these values were much smaller than the difference in the ECSA between with and without an ionomer.


S5 XPS analysis of the electrode with $\mathrm{CHF}_{3} \mathrm{SO}_{3}(\mathrm{C} 1)$.

The figure shows the F1s spectrum of the electrode before (a) and after (b) the electrochemical measurement (dipping the electrode into electrolyte solution). From the X-ray photoelectron spectroscopy (XPS) measurement of the electrode with C1 based on the F1s signal, the mass amount of C1 (trifilic acid) became $1 / 30$ of the initial amount after the electrochemical measurement. This amount corresponds to a 1-2 nm thickness if the density of C 1 is the same as Nafion. Furthermore, it means that the electrolyte solution can penetrate into the pores. In this experiment system (thin layer electrode), if the electrolyte solution contacts the surface of the platinum particles in the pores, the catalyst would become active for the ORR.


