Supporting Information

## Oxygen reduction reactivity of precisely controlled nano-structured model catalysts

Ken'ichi Kimijima<sup>†</sup>, Akari Hayashi<sup>†,‡</sup>, Shun Umemura<sup>†</sup>, Junichi Miyamoto<sup>†,#</sup>, Koshi Sekizawa<sup>§</sup>, Toshihiko Yoshida<sup>§</sup>, Ichizo Yagi<sup>†,\*</sup>

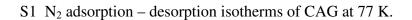
<sup>†</sup>Polymer Electrolyte Fuel Cell Cutting-Edge Research Center (FC-Cubic), National Institute of Advanced Industrial Science and Technology (AIST) 2-3-26 Aomi, Koto-ku, Tokyo 135-0064, Japan

<sup>‡</sup>Center for Fostering Young and Innovative Researchers, Nagoya Institute of Technology Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

<sup>§</sup>TOYOTA MOTOR CORPORATION, 1200 Mishuku, Susono, Shizuoka-ken 410-1193, Japan

<sup>#</sup>Current address: Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan

\* Corresponding author: Tel.: +81-3-3599-8551; fax: +81-3-3599-8554; E-mail address: i-yagi@aist.go.jp



0.6

400

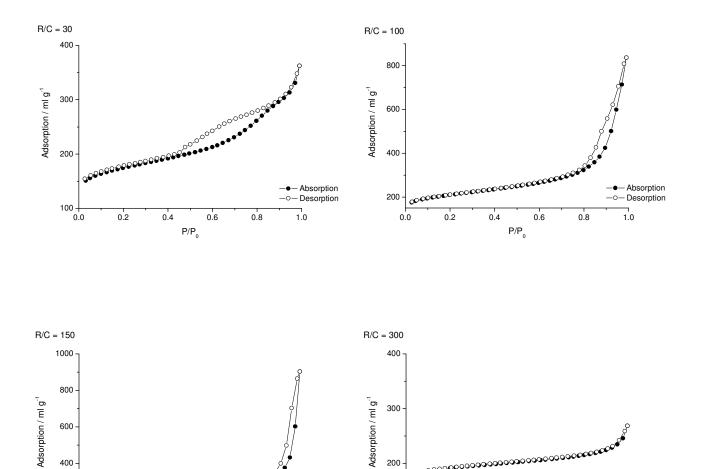
200 -

0.0

0.2

0.4

P/P<sub>0</sub>





,000000000000

0.6

P/P<sub>0</sub>

0.8

−●− Absorption −○− Desorption

1.0

0.2

0.4

200

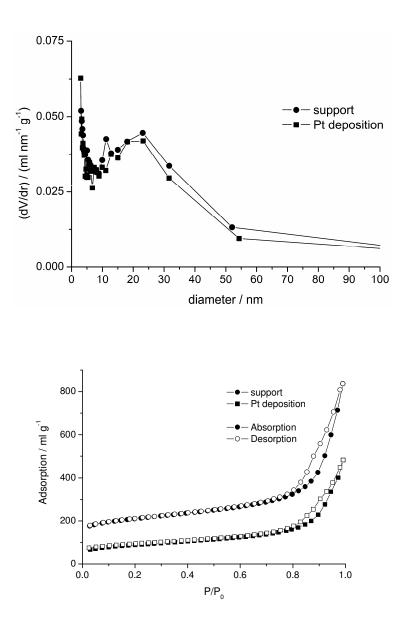
100 <del>|</del> 0.0

-•- Absorption -o- Desorption

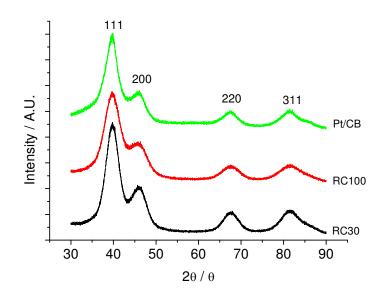
1.0

0.8

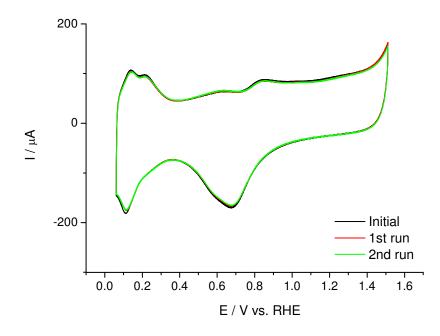
S2 Obtained pore distributions using BJH method from  $N_2$  adsorption isotherm of CAG support (R/C = 100, before deposition) (•) and RC100 (after platinum deposition) (•) (upper graph), and  $N_2$  adsorption – desorption isotherms at 77 K (lower graph).



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



Cyclic voltammograms of thin film electrode of RC100 without any ionomer under Ar saturated 0.1 mol dm<sup>-3</sup> HClO<sub>4</sub> solution at room temperature. The amount of platinum on the electrodes was 2.8  $\mu$ g (14  $\mu$ g cm<sup>-2</sup>). The sweep rate was 50 mV s<sup>-1</sup>. The electrochemical surface areas slightly changed, and were 36.8 (initial: before RDE measurement), 35.7 (1<sup>st</sup> run: after 1<sup>st</sup> RDE measurement), and 35.2 m<sup>2</sup>/g (2<sup>nd</sup> run: after 2<sup>nd</sup> RDE measurement). The ECSAs decreased a few percent after the measurement (RDE), *i.e.*, 3.0 % (1<sup>st</sup> run) and 4.3 % (2<sup>nd</sup> 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.



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 C1 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.

