

Supporting Information

A Kinetic Approach to Investigate the Mechanistic Pathways of Oxygen Reduction Reaction on Fe-Containing N-Doped Carbon Catalysts

Azhagumuthu Muthukrishnan¹, Yuta Nabae², Takeyoshi Okajima¹,

Takeo Ohsaka^{1,}*

¹Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, G1-5, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan.

²Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8552, Japan.

E-mail: ohsaka@echem.titech.ac.jp (T. Ohsaka)

Koutecký-Levich analysis

The RRDE voltammograms were analysed using the Koutecký-Levich equation as shown below

$$\frac{1}{i_D} = \frac{1}{i_k} + \frac{1}{i_{DL}} \quad (S1)$$

where i_k is the kinetic current density at a given potential and i_{DL} can be estimated from the Levich equation ($i_{DL} = 0.62nFD_{O_2}^{2/3}\nu^{-1/6}C_{O_2}^b\omega^{1/2}$; F is the Faraday constant, D_{O_2} and $C_{O_2}^b$ are the diffusion coefficient (1.4×10^{-5}) and bulk concentration (1.13×10^{-6} mol cm³) of O₂ dissolved in solution, respectively, ν is the kinematic viscosity of the solution (0.01 cm² s⁻¹) and ω is the rotational speed). The $1/i_D$ vs. $\omega^{-1/2}$ plots are linear at mass-transport limiting region (at 0.1 V vs. RHE) as shown in Figure S1(A) for various loading densities of Fe-N-C catalysts. The i_k is estimated from the intercept of the $1/i$ vs. $\omega^{-1/2}$ (Koutecký-Levich) plot, which increases with increasing the loading density (Table S1). The number of electrons (n), estimated from the slope of the Koutecký-Levich plot, increases with increasing the loading density and is found to be very close to 4 at 300 µg/cm². The i_k values at higher loading densities indicate that the ORR is solely controlled by the mass-transport of O₂ molecules to the electrode surface. As shown in Figure S1(A), the experimental plots give almost the same slope as expected for 4-electron ORR.

A similar methodology is adopted for the N-C catalyst to estimate the i_k and n at various loading densities. At low loading density (40 µg cm⁻²), n is close to 2 whereas the value of n is increased to 3.8 at 300 µg/cm². Also, i_k value increases with increasing the loading density. The values of n and i_k are summarized in the Table S1 for both Fe-N-C and N-C catalysts. The i_k value of the Fe-N-C catalyst is 3.3 times larger than that of the N-C catalyst at 40 µg cm⁻². However, this difference is decreased at high loading density, i.e., at 300 µg cm⁻², is

only 1.6 times, indicating the increased ORR performance. It can be seen from Figure S1(B) that the plot at the low loading density (e.g., 40 $\mu\text{g cm}^{-2}$) gives the slope close to that obtained for the 2-electron reduction and the slopes close to that expected for the 4-electron reduction are obtained at the loading densities greater than 200 $\mu\text{g cm}^{-2}$.

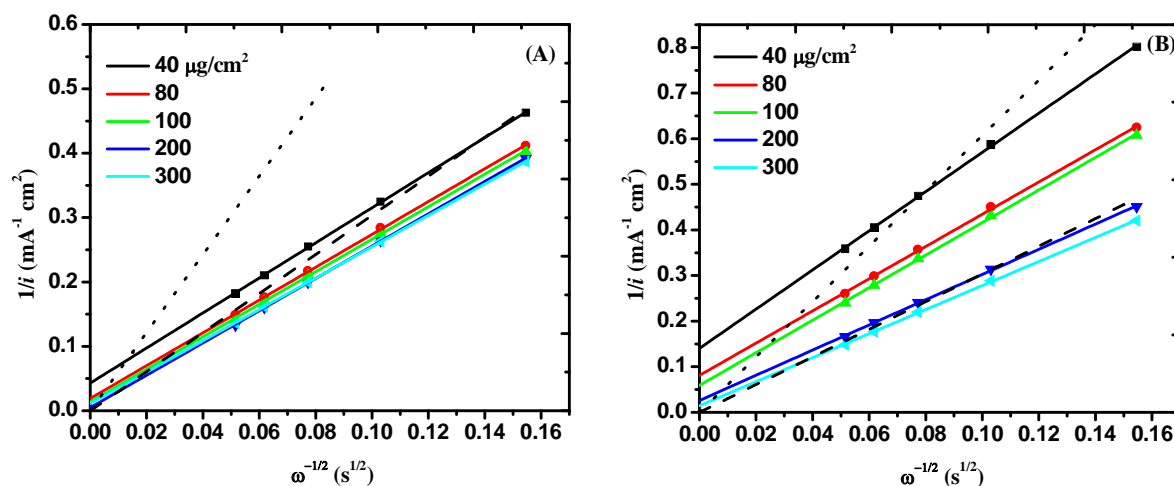


Figure S1: Koutecký-Levich plots for the Fe-N-C (A) and N-C (B) catalysts at the limiting current region (0.1 V) for various loading densities. The theoretical plots for the 4-electron (dashed line) and the 2-electron (dotted line) reduction of oxygen are shown.

Table S1. Values of n and i_k for the Fe-N-C and N-C catalysts at various loading densities.

Loading density($\mu\text{g/cm}^2$)	Fe-N-C		N-C	
	n	i_k (mA cm^{-2})	n	i_k (mA cm^{-2})
40	3.7	23.3	2.3	7.1
80	3.9	52.4	2.8	12.3
100	4.0	71.9	2.8	16.9
200	4.0	128.7	3.6	38.5
300	4.1	107.3	3.8	68.9

Evaluation of ORR rate constants at zero loading density

To estimate the rate constants at zero loading density we have employed a method of plotting the loading density vs. rate constant, i.e., a linear fitting of such plots leads to the intercepts which are referred to as rate constants at zero loading density. The loading density normalised rate constants (k_1/Γ , k_2/Γ and k_3/Γ) for the Fe-N-C and N-C catalysts are shown in Figures S2 and S3, respectively.

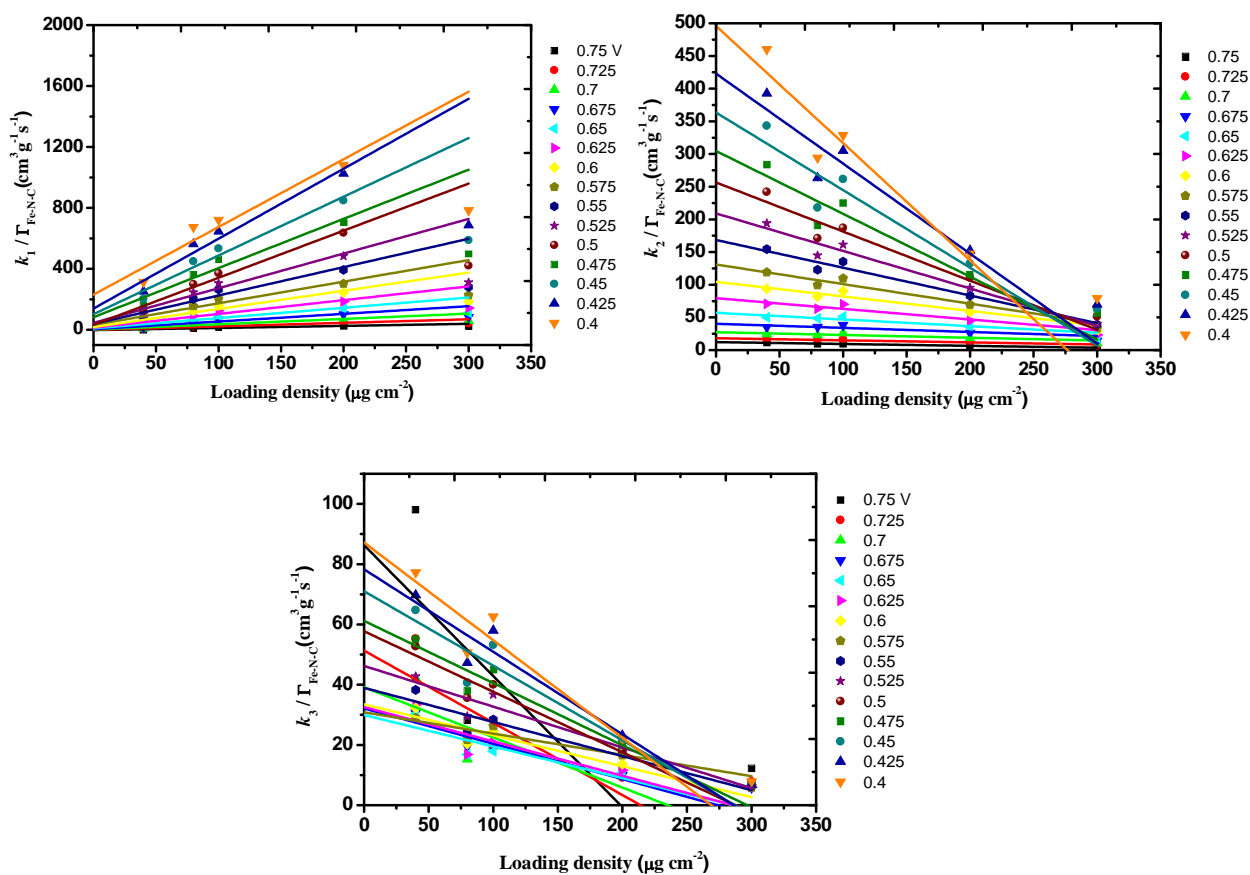


Figure S2: The loading density dependence of the loading density-normalised rate constants ($k_i/\Gamma_{\text{Fe-N-C}}$) for the individual rate constants for the Fe-N-C catalyst.

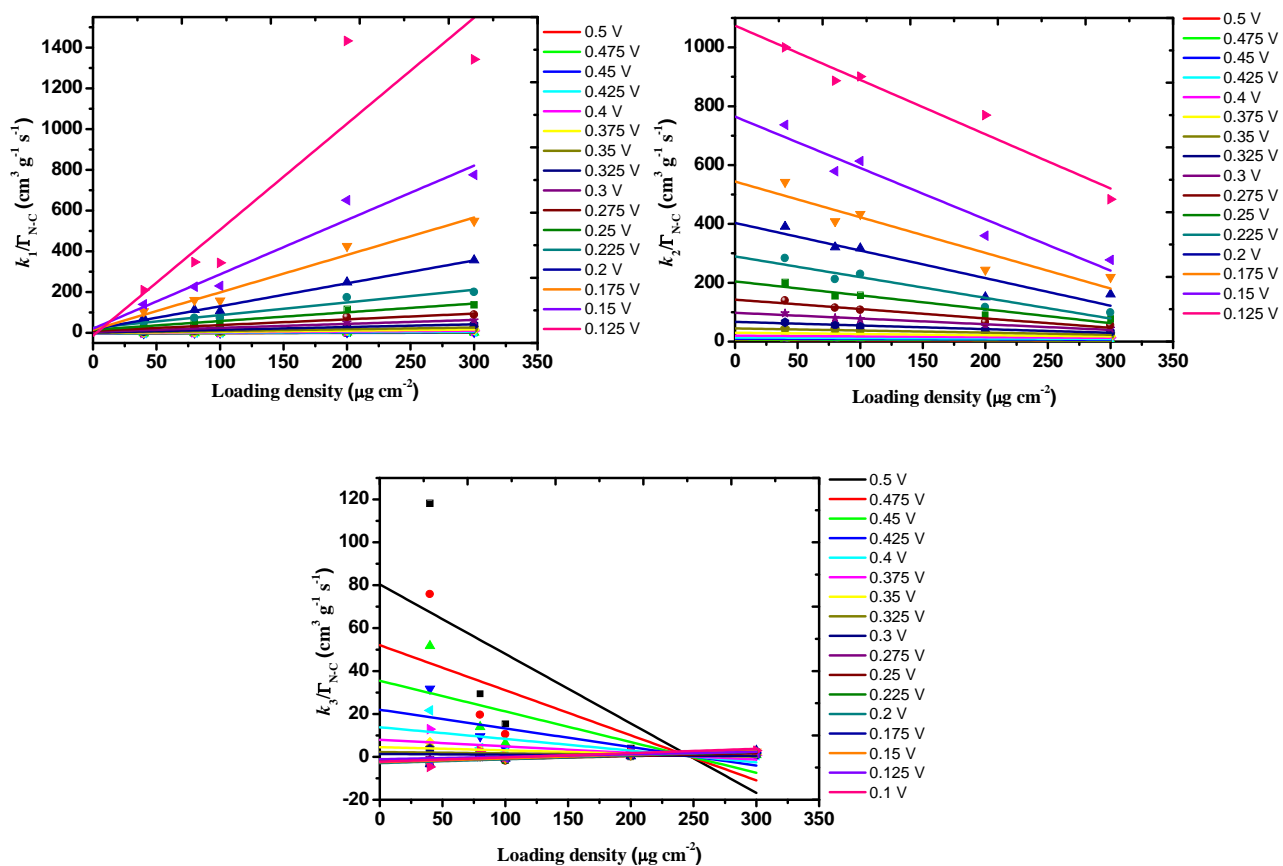


Figure S3: The loading density dependence of the loading density-normalised rate constants (k_i/Γ_{N-C}) for the individual rate constants for the N-C catalyst.

Estimation of H_2O_2 -disproportionation rate constants

Methodology for the estimation of disproportionation rate constant of H_2O_2 has been already established by Jaouen and Dodelet [*J. Phys. Chem. C* **2009**, *113*, 15422-15432]. Briefly, a known amount (2 mg) of each of the catalysts was added to the known volume (50 mL) of O_2 -saturated 0.1 M HClO_4 and the solution was stirred with a uniform distribution of the catalyst. 51.1 μL of 30% H_2O_2 was added to the solution, resulting in an initial H_2O_2 concentration of 10 mM. Immediately after addition of H_2O_2 , the RRDE voltammetric diffusion-limited current ($I_{\text{DL,t}}$) was measured at constant intervals with the Pt/C electrode

(the loading density of the Pt/C electrode is $37.2 \mu\text{g}/\text{cm}^2$) at 1600 rpm rotational speed. The RRDE voltammogram was also measured before the addition of H_2O_2 in the O_2 -saturated solution and the obtained time-independent current limited by O_2 diffusion is mentioned as I_{DL,O_2} . Finally, the time-dependent H_2O_2 diffusion-limited current ($I_{\text{DL},\text{H}_2\text{O}_2}$) was calculated as follows

$$I_{\text{DL},\text{H}_2\text{O}_2} = I_{\text{DL},t} - I_{\text{DL},\text{O}_2} \quad (\text{S2})$$

The rate constants (k_4) of the homogeneous disproportionation reaction of H_2O_2 can be calculated from $\log(I_{\text{DL},\text{H}_2\text{O}_2})$ vs. time plots as shown in Figure S4. The slopes for the both catalysts gave the values of k_4 .

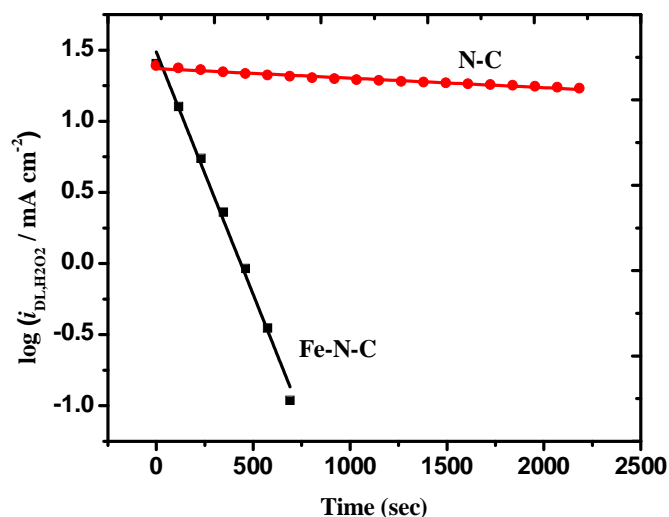


Figure S4. $\log(I_{\text{DL},\text{H}_2\text{O}_2})$ vs. time plots for Fe-N-C and N-C catalysts. The rotating disk electrode voltammetry was carried out using the Pt/C-coated GC electrode (the coating amount of Pt/C: $37 \mu\text{g cm}^{-2}$) at potential scan rate of 20 mV s^{-1} and electrode rotation speed of 1600 rpm in O_2 -saturated 0.1 M HClO_4 solution containing $10 \text{ mM H}_2\text{O}_2$ in the presence of each catalyst of 2 mg . The $I_{\text{DL},\text{H}_2\text{O}_2}$ values were taken at 0.2 V .

To compare the thus-estimated disproportionation rate constants with the ORR rate constants, the unit (cm s^{-1}) of k_1 , k_2 and k_3 needs to be converted to the same unit of the homogenous rate constant (k_4) by taking into account the thickness (l) of the catalyst coated

on the electrode. The ORR rate constants divided by the thickness of the film leads to the unit of s^{-1} . The thickness of the film coated on the GC surface was estimated as $23 \pm 3 \mu m$ using 3D laser Scanning Microscope (Keyence Co., Japan). Finally, the k_1/l , k_2/l and k_3/l are calculated as 95.7, 12.8 and $1.9 s^{-1}$, respectively, for the Fe-N-C and 126.1, 66.9 and $0.2 s^{-1}$, respectively, for the N-C catalyst. The k_4 is normalized by the amount of the catalyst coated on the electrode for the comparison and the estimated values are 9.2×10^{-5} and $2.0 \times 10^{-6} s^{-1}$ for Fe-N-C and N-C catalysts, respectively. These values are very low compared with the k_1/l , k_2/l and k_3/l and hence the disproportionation of H_2O_2 is negligible. From the mechanistic point of view it is expected that k_4 might influence on k_3 , but not on k_1 and k_2 . As mentioned above, k_4 is too small compared to the k_3 . [Wu *et al.* Langmuir **2015**, *31*, 5529-5536] Hence the catalytic disproportionation reaction of H_2O_2 on these catalysts is considered to be very slow and it is negligible.

Wroblowa model

The RRDE voltammetric equations are derived by Damjanovic *et al.* for the evaluation of the rate constants (k_1 , k_2 and k_3) for a model of ORR shown in Scheme 1 and are expressed as follows.

$$\frac{I_D}{I_R} = \frac{1}{N} \left[\left(1 + 2 \frac{k_1}{k_2} \right) + \left(\frac{2k_3 \left(1 + \frac{k_1}{k_2} \right)}{Z_{H_2O_2}} \right) \omega^{-1/2} \right] \quad (S3)$$

$$\frac{I_{DL}}{I_{DL} + I_D} = 1 + \frac{k_1 + k_2}{Z_{O_2}} \omega^{-1/2} \quad (S4)$$

$$\text{with } Z_{H_2O_2} = 0.2 D_{H_2O_2}^{2/3} \nu^{-1/6} \text{ and } Z_{O_2} = 0.2 D_{O_2}^{2/3} \nu^{-1/6}$$

where I_D is the disk current, I_R is the ring current, I_{DL} is the disk limiting current, ω is the rotational speed of electrode, N is the collection efficiency, $D_{H_2O_2}$ and D_{O_2} are the diffusion coefficients of H_2O_2 and O_2 , respectively and ν is the kinematic viscosity of the solution used. By combining the intercepts and slopes of both I_D/I_R vs. $\omega^{-1/2}$ and $I_{DL}/(I_{DL} - I_D)$ vs. $\omega^{-1/2}$ plots, the individual rate constants are obtained.

By taking into account the adsorption equilibrium between the adsorbed and desorbed H_2O_2 near the disk electrode surface, Wroblowa et al. derived the RRDE voltammetric equations for the model for ORR shown in Scheme 2. A liner plot of $I_{\text{DL}}/(I_{\text{DL}}-I_{\text{D}})$ vs. $\omega^{-1/2}$, which was confirmed actually in the present case, indicates that k_4 is negligibly small and the relation between $I_{\text{DL}}/(I_{\text{DL}}-I_{\text{D}})$ and $\omega^{-1/2}$ is exactly the same as equation (S4) and the $I_{\text{D}}/I_{\text{R}} - \omega^{-1/2}$ relation is expressed by the following equation:

$$\frac{I_{\text{D}}}{I_{\text{R}}} = \frac{1}{N} \left[\left(1 + 2 \frac{k_1}{k_2} \right) + A + \left(\frac{Ak_6}{Z_{\text{H}_2\text{O}_2}} \right) \omega^{-1/2} \right] \quad (\text{S5})$$

where $A = \frac{2k_1k_3}{k_2k_5} + \frac{2k_3}{k_5}$. The intercept and slope of $I_{\text{D}}/I_{\text{R}}$ vs. $\omega^{-1/2}$ plot according to equation (S5) are

$$J = \frac{1}{N} \left(1 + 2 \frac{k_1}{k_2} + A \right) \quad (\text{S6})$$

and

$$S = \frac{1}{N} \left(\frac{Ak_6}{Z_{\text{H}_2\text{O}_2}} \right), \quad (\text{S7})$$

respectively. The relation between J and S is given by

$$NJ = \left(1 + 2 \frac{k_1}{k_2} \right) + \frac{Z_{\text{H}_2\text{O}_2}}{k_6} NS \quad (\text{S8})$$

Finally, some important conclusions have been drawn from the NJ vs. NS plots.

If $k_1 = 0$ and the plot is linear, the intercept of the NJ vs. NS plot must be unity. In that case, the ORR is considered to follow the sequential mechanism.

If k_1 is not equal to zero (i.e., the intercept is greater than unity) and the plot is still linear, k_1 and k_2 have similar potential dependence. The values of k_6 and k_1/k_2 can be estimated from the slope and intercept, respectively.

If k_1 is not equal to zero and the plot is not linear, k_1 and k_2 are different functions of potential.