Effect of the N content of Fe/N/Graphene catalysts for the oxygen reduction reaction in alkaline media

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Supplementary Information

X-ray diffractograms of Fe/NG catalysts

Fig. S1. X-ray diffractograms of Fe/N/G samples with different N/C ratios
A comparison of the catalytic performance for the ORR in KOH of pristine graphite nanoplates (black lines), Fe/N/G-0.3 (green lines) and a commercial Pt/C catalyst purchased from Johnson Matthey (Pt loading 40wt.%) measured under identical reaction conditions as shown in the caption to the figure is shown in Fig S2. As observed, the ORR activity of the pristine nanoplates is significantly lower than that of the Fe/N/G-0.3

Fig S2. ORR polarization curves and ORR mass activities in 0.1 M KOH at 10 mVs⁻¹ and 1600 rpm for Pt/C 40 wt. % and pristine graphite nanoplates. For the sake of comparison, the ORR polarization curve and ORR mass activity of the best catalyst of the series (Fe/N/G-0.3) is also included. Catalyst loading: 0.06 mg_cat/cm² for Pt/C catalyst and 0.6 mg_cat/cm² for graphite nanoplates and Fe/N/G-0.3 samples.
Evaluation of H\textsubscript{2}O\textsubscript{2} production from Rotating Ring Disk Electrode

H\textsubscript{2}O\textsubscript{2} production was evaluated by using a rotating ring disk electrode (RRDE) (with a Pt ring), under the same experimental conditions than that reported above for the RDE applying a constant ring potential of 1.2 V. The fraction of H\textsubscript{2}O\textsubscript{2} produced was calculated as shown in Equation 1

\[ X_{H2O2} = \frac{2i_R}{N} \frac{N}{i_D + i_R} \quad (Eq. 1) \]

where \(i_D\) is the disk current and \(i_R\) is the ring current. Ring efficiency (N) is of 26%.

The number of exchanged electrons was calculated from Equation 2

\[ ne = 4 - \frac{96H_2O_2}{50\%} \quad (Eq. 2) \]

![Graph showing H\textsubscript{2}O\textsubscript{2} production in 0.1 M KOH at 10 mVs\textsuperscript{-1} and 1600 rpm for Fe/N/G-0.3 (black line) and Fe/N/G-0.6 (red line). Catalyst loading 0.6 mg\textsubscript{cat}/cm\textsuperscript{2}](image)

In addition, the average number of exchanged electrons during the ORR can be determined from the relationship between the \(i_0\) and the rotation rate as defined by the Levich equation:

\[ i_0 = 0.201nFC_{O2}D_{O2}^{2/3}v^{-1/6} \omega^{1/2} \]

Where \(n\) is the ORR overall electron transfer number, \(F = 96487 \text{ C} \cdot \text{mol}^{-1}\) is Faraday’s constant, \(C_{O2} = 1.1 \times 10^{-6} \text{ mol} \cdot \text{cm}^{-3}\) is the concentration (or solubility) of O\textsubscript{2} in the electrolyte solution, \(D_{O2} = 1.9 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}\) is the diffusion coefficient of O\textsubscript{2}, \(v = 1 \times 10^{-2} \text{ cm}^2 \cdot \text{s}^{-1}\) is the viscosity of the
KOH aqueous solution, and $\omega$ is the electrode rotating rate (rpm). According with the parameters for a KOH solution of 0.1M [1]

Fig S4. Linear sweep (10 mV/s) recorded in O₂-saturated in 0.1M KOH at different rotation rates and Levich-Koutecky plots for the Fe/N/G-0.6 and Fe/N/G-0.3 at 0.2V (*), 0.4V (●), 0.6V (◊) and 0.7V (○). The insets to the figures are the number of electrons obtained from the Levich-Koutecky equation.
Stability of catalysts

**Fig S5.** 1st and 50th cyclic voltammogram recorded in Ar-saturated KOH solution.

**References**