Supplementary Information

How many surface atoms in Co_3O_4 take part in oxygen evolution? Isotope labeling together with differential electrochemical mass spectrometry

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Calculations for the Co_3O_4 (50 nm) catalyst with 200 µg cm^{-2} loading in 0.1M LiOH solution (upper potential limit is 1.8V):

Analysis of the real surface area of the catalyst using the ball model, DL-capacitance assumption model and redox peak model was performed and compared to BET data:

Based on the model used in eq. 7, the number of moles of oxygen atoms at surface per true cm^2 is S = 1.85 nmol /cm^2_{geo}.

- *Isotope exchange model*:

For the 50 nm particles, the total amount of exchanged lattice oxygen is $n_{ex,t}$ = 7.3 nmol/cm^2. This gives a true surface area per geometric area of $A_{tr}/A_{geo\ r}$= 7.3 (nmol/cm^2_{geo})/1.85 (nmol/cm^2_{tr})= 3.9 $cm^{2/}cm^2$.

Here, the total amount of oxygen atoms in the loading is $n_t\,(O^{2-})$ = 3320 nmol/cm^2. Therefore, the amount of exchanged oxygen to the total loading is r_{ex}= 7.3 (nmol/cm^2)/3320 (nmol/cm^2)= 0.22%.

- *ball model*:

For radius r = 25 nm, the mass of this loading is $m(Co_3O_4)$ = 56.6 µg and with the help of eq. 8, this gives a true surface area of A_{tr}= 11 cm^2. This means the A_{tr}/A_{geo}= 11 cm^2_{tr}/ 0.283 cm^2_{geo}= 39 cm^2_{tr}/cm^2_{geo}, and the number of moles of surface atoms according to eq. 9 is n = 39 (cm^2/cm^2) × 1.85 (nmol/cm^2)= 72 nmol/cm^2_{geo}.

According to eq. 6, the fraction of oxygen exchanged from surface atoms y_{ex}= 7.3/ 72 = 0.1 (10%).

- *DL- capacitance method*:

For the potential range between 0.76 V and 1.39 V, using eq. 10 we obtain A_{tr}/A_{geo}= 140 cm^2_{tr}/cm^2_{geo}. Thus, the true surface area is A_{tr}= 140 × 0.28 cm^2 /56.6 µg= 70 m^2/g. The number of moles of surface atoms according to eq. 9 is n= 140 (cm^2/cm^2) × 1.85 nmol/cm^2_{tr}= 255 nmol/$cm^2_{geo.}$

- *Redox peak model*:

The charge under the redox peak corresponding to the transition $Co^{3+}/Co^{4+/3+}$ is 5.7 mC/cm^2. Consequently, the number of moles of surface atoms is n_{surf} = *5.7/(1.F)* nmol/cm^2= 59 nmol/cm^2, this gives that the amount of exchanged oxygen to the surface atoms is y_{ex}= 12%. Using eq. 9, we obtain A_{tr}/A_{geo}= 59(nmol/cm^2_{geo})/1.85 (nmol /cm^2_{tr}) = 32 cm^2_{tr}/cm^2_{geo}.

BET and XRD data of Co_3O_4

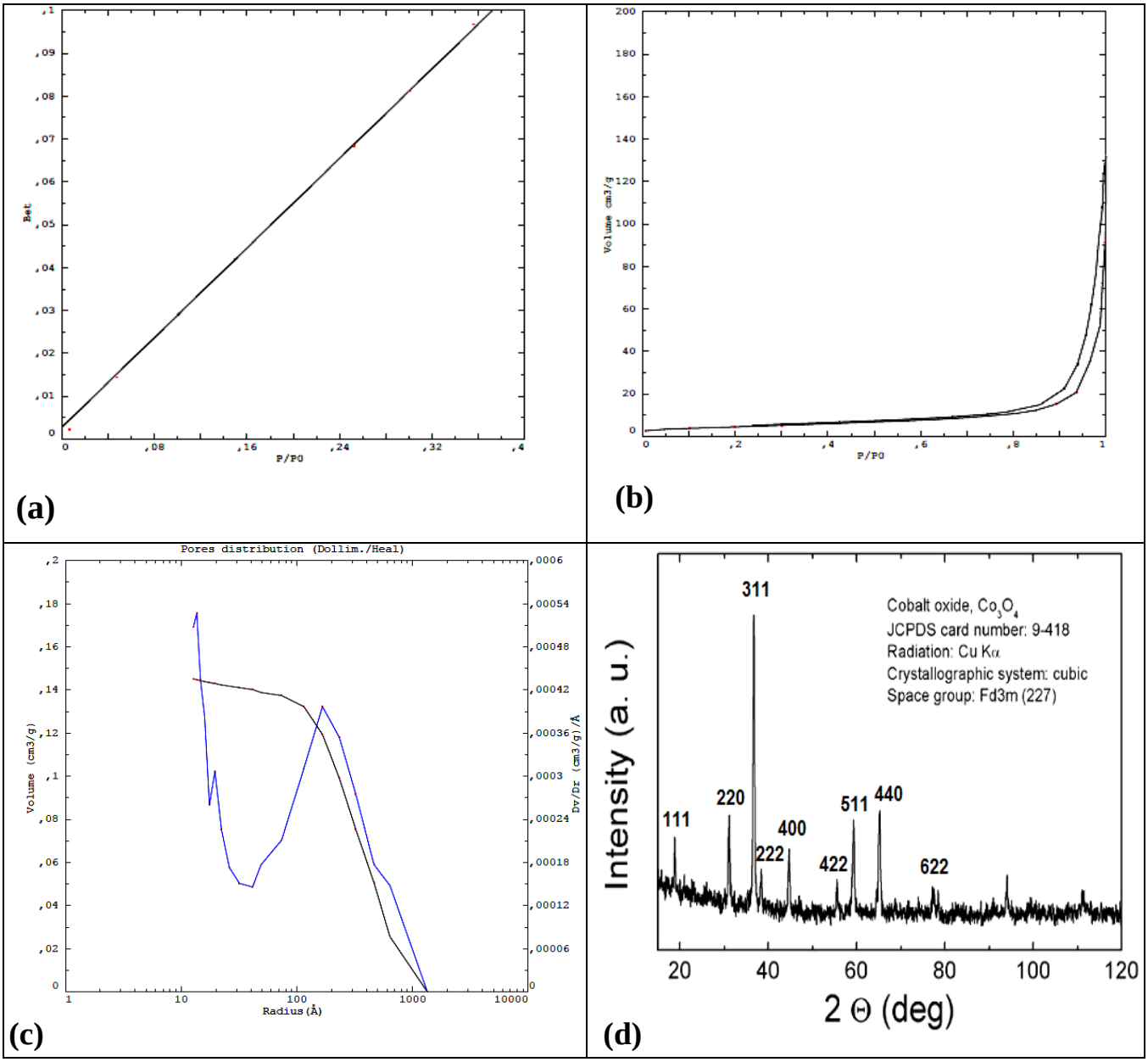

Fig. S1. (a) BET plot of Co_3O_4 (50 nm) catalyst. (b) Adsorption/desorption isotherms on the catalyst. (c) Particle size distribution of the corresponding catalyst. (d) XRD patterns of Co_3O_4 (50 nm).

BET plot and adsorption/desorption isotherms for Co_3O_4 catalyst are depicted in Fig. S1a and b. The specific surface area obtained for 50 nm Co_3O_4 catalyst is 16.5 m^2 g^{-1}. The particle size distribution of Co_3O_4 was analyzed and the average particle size (assuming that the particles are spherical and non-porous) was determined from BET data. An average particle diameter of 40 nm was found as shown in Fig. S1c, which is consistent with the value given from the manufacturer data sheet. XRD patterns (supplied from the manufacturer) of Co_3O_4 (50 nm) catalyst are shown in Fig. S1d. The signals are then analyzed and assigned to the different phases of cobalt oxide. The graph exhibits intense and sharp diffraction peaks which are

characteristic of the Co_3O_4 cubic spinel crystalline structure. The signals of Co_3O_4 agreed perfectly with XRD standard data (JCPDS card number: 9-418). The oxide is highly pure since no peaks of any impurity phase could be observed from this pattern.