Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Electrophoretic Deposition Improves Catalytic Performance of Co_3O_4 Nanoparticles for Oxygen Reduction/Oxygen Evolution Reactions

M. Fayette, A. Nelson, and R.D. Robinson

Calculation of deposited mass in EPD

The sensitivity factor of the quartz crystal as calculated from the Sauerbrey equation[1], 56.6 Hz μg^{-1} cm^2, is corrected for the area of the substrate (1.37 cm^2 for the EQCM crystal electrode), then inverted to identify the mass sensitivity:

$$(56.6 \text{ Hz ug}^{-1} \text{ cm}^2 \text{ x } 1 \text{ ug/1000ng}) / 1.37 \text{ cm}^2 = 0.0413 \text{ Hz ng}^{-1}$$

$$1/ 0.0413 \text{ Hz ng}^{-1} = 24.2 \text{ ng Hz}^{-1}$$

At t = 30 s, the EQCM records an average Δf of -2600 Hz, corresponding to a loading of 62361.6 ng. Correcting for the active area of the EQCM electrode gives a loading of 45519.4 ng cm^{-2}. This value is then multiplied by the area of the GC electrode (0.2 cm^2) to give the total mass loading of 9.2 µg used in the rest of the work. The fluctuating frequency accordingly gives a variance in this mass of about ±2 ug. As mentioned in the main text, however, the EPD current is highly reproducible.

Calculation of Ag coverage

To demonstrate, we integrate a chronamperometric curve (not shown) to derive a total deposition charge *Q* for Ag of about 5 mC. From the geometric area of the substrate and the monolayer charge for Ag on GC (0.2 mC/cm^2)[2] we determine a monolayer charge for the substrate Q_{Ag} of about 0.04 mC. Thus, the total number of monolayers of Ag deposited for this example is estimated to be $Q/Q_{Ag} = 125$. Roughness of the silver substrate on which UPD is performed expected on the GC surface due to lack of wetting ability, but it was found later in FE-SEM that roughness of the silver layer on the Co_3O_4 particles is minimal due to possible hetero-epitaxial growth (see main text). As such, we feel it is not necessary to introduce a correction factor. Based on the case where 5 mC charge is passed depositing Ag on GC, the actual surface area of the GC is calculated by Pb UPD to be ~1.5-2× the geometric area. Considering that the GC substrate is amorphous, the deposition on the crystalline NPs should (and was found to) result in a smoother surface due to initial 2-D growth[3]; the roughness factor is therefore left out of the following measured surface areas.

Verification of the amount of Ag deposited

LSV was employed in order to verify that an appropriate amount of Ag was electrodeposited onto the NPs (Fig. S1). This method is used to verify that the surface area determined by the Pb UPD is reasonable (vis-à-vis enough Ag deposited on the surface). During the initial application of potential in the Ag deposition step, Co_3O_4 is being reduced at the same time that Ag is being deposited. These competing processes result in the integrated current during the deposition process not accurately accounting for the amount of Ag deposited. It can be seen, however, that the Ag dissolution peak is quite positive and is also the only peak in the voltammogram, indicating that the Co NP surface beneath is not exposed as additional peaks would be present in the voltammogram (Fig. S1). Ideally, as the Ag dissolves, the Co should re-oxidize to Co_3O_4 or possibly CoO_2[4], as the onset of OER is slightly more positive relative to the Ag oxidation potential in solution, so there should be no peaks due to NP dissolution. The charge associated with the peak in Figure 7 is within the range of 2-4 mC for both EPD and dropcast films, meaning that there is adequate coverage of the NP with Ag (about ~10-20 monolayers of Ag based on the charge density of Ag and the calculated surface area of the catalysts), which should ensure accurate determination of the surface area.

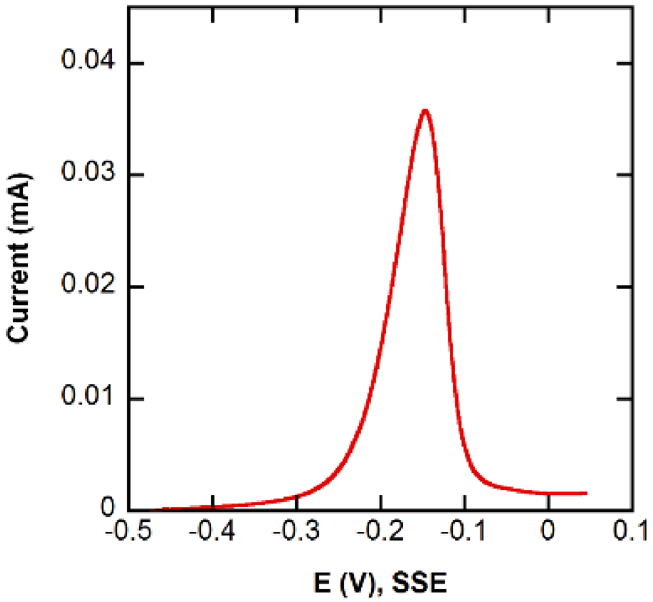

Figure S1: Ag dissolution on EPD Co_3O_4 NP thin film on GC. Solution: 0.1 M $NaClO_4$ + 0.5 M NH_4OH. Scan rate: 1 mV/s.

Theoretical surface areas

Surface area of the catalysts is calculated based on the initial number of particles deposited. Based on the small mass of the encapsulating ligands it is assumed that they may be ignored in the mass loading. The theoretical density[6] ρ of ε-Co based on the crystal structure is 8.635 g cm^{-3}, giving an approximate particle concentration of $1.8 \cdot 10^{11}$ particles per μg of loading by determining particle mass $M_{particle}$ from volume $V_{particle}$:

$$M_{particle} = \rho \text{ x } V_{particle} = 8.635 \text{ g cm}^{-3} \text{ x } 4/3\ \pi\ (5.35 \text{ x } 10^{-7} \text{ cm})^3 = 5.5 \text{ x } 10^{-18} \text{ g per particle}$$

After oxidation the particles grow from 10.7 nm to 14.8 nm in diameter while remaining roughly spherical; we then estimate their surface area $A_{particle}$ for the following mass loadings, since we know the particle counts.

$$A_{particle} = 4\ \pi\ (7.4 \text{ x } 10^{-7} \text{ cm})^2 \text{ x } 1.8 \text{ x } 10^{11} \text{ particles } \mu\text{g}^{-1} = 1.24 \text{ cm}^2 \text{ ug}^{-1}$$

The true particle radius, of course, corresponds to the coated Co_3O_4 particle and not the bare one, and it may be as much as a few nanometers larger based upon the thickness of the Ag layer. It is not a simple matter to calculate the exposed area of a sphere inside an assemblage with varying packing ratios, so we have made a simplifying assumption: if the spheres were instead cubes, at least one face will be blocked, either because it attaches to the substrate or because it attaches to another particle. Thus the theoretical surface area is calculated as if the particles were cubes with 1/6 of their surface area made inaccessible.

Table S1. Theoretical and measured surface area for NP films.

Loading	Total number of ε-Co particles deposited(x10^{12})	Theoretical surface area of Co_3O_4 (cm^2)	UPD surface area (cm^2) [average]	Average surface area per mass (cm^2 ug^{-1})
5 µg (dropcast)	0.9	5.18	1.12-1.90 [1.45] N=5	0.29
9.2 µg (EPD)	1.6	9.43	0.78-0.95 [0.87] N=4	0.10
10 µg (dropcast)	1.8	10.35	1.04-2.75 [1.65] N=8	0.17
Ideal bare particle area				1.04

Comparison to the work of Bromberg et. al.[7]

Previously an area of 5.6 cm^2 was reported for a NP film consisting of 20 ug of Pt_4Cu cubes having an edge length of 8.0 nm. Based on the assumption that the cubes have the density of Pt and that a single side faces the substrate and is not accessible, it was concluded that the theoretical area of the film is about 5.8 cm^2; thus about 97% of the theoretical area of the film is discovered by hydrogen UPD. Refining this estimate by weighting the density according to the true formula weight of the intermetallic gives a theoretical area of 6.7 cm^2, bringing the "discovery ratio" or correction factor down to about 83%. For comparison, the discovery ratio reported in this work is about 16% for dropcast films and falls to 10% for EPD films. To illustrate: if a cube film had the same theoretical area as a 10 µg dropcast film (10.3 cm^2), applying the second correction factor estimates the hydrogen UPD area to be about 8.6 cm^2, much more than the reported result for 10 µg dropcast films or 9.2 µg EPD films.

Additionally, we note that the discovery ratio appears to increase at lighter mass loadings. A possible explanation may lie in the relative behavior of dropcast aggregate formation compared to EPD. The material in dropcast solution tends to form a single aggregate visibly localized on the surface of the electrode, while EPD films are smooth and homogeneous. Since the volume of an aggregate will grow more quickly than its surface area (which is preferentially exposed to Ag deposition and UPD), an increasing amount of material is "hidden" from the UPD method with higher mass loadings. By making the amount of mass deposited smaller, the surface area of the aggregates is increased and the discovery ratio thus increases.

References

1. G. Sauerbrey, *Z. Physik*, 1959, **155**, 206-222.

2. C. Palacio, P. Ocón, P. Herrasti, D. Díaz and A. Arranz, *Journal of Electroanalytical Chemistry*, 2003, **545**, 53-58.
3. E. B. Budevski, G. T. Staikov and W. J. Lorenz, *Electrochemical Phase Formation and Growth: An Introduction to the Initial Stages of Metal Deposition*, Wiley, 2008.
4. Y. Liang, H. Wang, P. Diao, W. Chang, G. Hong, Y. Li, M. Gong, L. Xie, J. Zhou, J. Wang, T. Z. Regier, F. Wei and H. Dai, *Journal of the American Chemical Society*, 2012, **134**, 15849-15857.
5. Y. Liu, S. Bliznakov and N. Dimitrov, *Journal of Physical Chemistry C*, 2009, **113**, 12362-12372.
6. D. P. Dinega and M. G. Bawendi, *Angewandte Chemie International Edition*, 1999, **38**, 1788-1791.
7. L. Bromberg, M. Fayette, B. Martens, Z. P. Luo, Y. Wang, D. Xu, J. Zhang, J. Fang and N. Dimitrov, *Electrocatalysis*, 2013, **4**, 24-36.