Nanoscale characterization of crystallinity in DSA® coating

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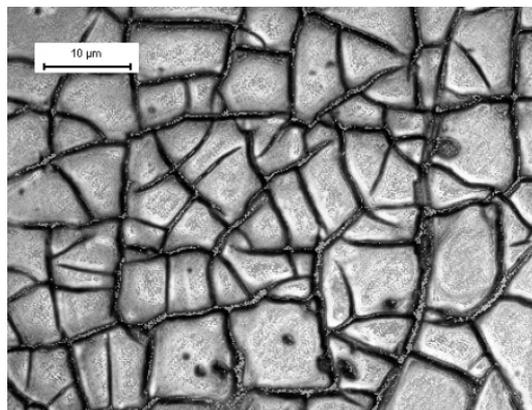[b] Permascand AB, Box 42, SE-840 10 Ljungaverk, Sweden
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Abstract Dimensionally Stable Anodes (DSA®) are used for industrial production of e.g. chlorine and chlorate. It is known that the superior electrocatalytical properties of DSA® is due to the large effective area of the porous coating. However, this knowledge is mainly found from in situ electrochemical measurements. Here, we used ex situ methods, AFM, TEM and gas porosimetry, for characterization at the nanoscale. The DSA® coating was found to consist of mono-crystalline grains with a size of 20-30 nm and with pores of about 10 nm in diameter. Using a simple geometrical model an effective area was calculated. For a typical coating thickness, an increase of about 1000 times in the effective surface area was found, which is consistent with in situ estimations. These results suggest that the dominating source of surface enlargement is due to nano-crystallinity.

1. Introduction

Dimensionally Stable Anodes (DSA®) are used for large-scale industrial production of, for example, chlorine and chlorate. A typical anode consists of a titanium substrate coated with a mix of titanium- and ruthenium dioxide ($Ti_{0.7}Ru_{0.3}O_2$). DSA® coatings has an effective surface area that is 10-1000 times larger than the visible surface [1]. However, the high increase in surface area cannot be explained by the cracked mud structure (Figure 1) alone. To directly measure this area is a difficult task [2] and instead in situ electrochemical methods have mainly been used [3]. We used here, a combination of atomic force microscopy (AFM), transmission electron microcopy (TEM) and gas porosimetry, and used these ex situ methods to estimate the effective surface area and to reveal the microstructure of the coating.


Figure 1 Light microscopy image of a DSA® coating. The superior electrocatalytical properties of the DSA® is due to its large effective area [1]. However, the high increase in surface area cannot alone be explained by the cracked mud structure visible in this image.

2. Experimental

For microscopy, commercial DSA$^®$ samples (Permascand AB) were used, while for porosimetry the electrode samples were prepared by coating titanium with a solution of $RuCl_3$ and $TiCl_4$. After drying and heating at 470°C a 4 μm thick catalytic coating resulted with a similar composition as that of the commercial ones. Imaging was done by light microscopy (Zeiss Axiotech Vario), AFM (Digital Instruments Dimension 3100), and TEM (JEOL 2000FX). The TEM samples were prepared by scraping of the coating by a sharp knife and the powder was placed on TEM grids (Carbon grid 400 mesh). The pore size distribution was measured using N_2 gas porosimetry (Micromeritics, ASAP 2010), where adsorption data was analyzed using the Barrett, Joyner and Halenda (BJH) model [4].

3. Imaging and diffraction

AFM imaging on top of the plaquettes showed a rough surface on the nanoscale (Figure 2), consistent with earlier findings [5]. TEM showed that this is not just a surface phenomenon, but the whole coating seems to be built up of 20-30 nm sized grains (Figure 3), and the bumps in the AFM images are the top of the grains visible in the TEM images. The grains were further studied by electron diffraction in the TEM. TiO_2 crystallizes in rutile (Figure 4a) and anatase structure. It is believed [1] that the Ru atoms can replace Ti atoms in the rutile structure. The diffraction pattern showed a rutile structure (Figure 4b and c). It is obvious that the grains are crystalline and it seems that they are mono-crystalline. The extra set of spots in the diffraction pattern (marked with an arrow) could be double diffraction as a result of a thick sample [6]. In this case 30 nm can be considered thick.

Figure 2 AFM image of a plaquette. 20 nm wide and 5 nm high grains are closely packed together all over the plaquette top surface.

Figure 3 TEM image of commercial DSA$^®$ coating. The whole coating consists of 20-30 nm-sized grains. (The black circle in the center is an imaging artifact.)

Figure 4 a) Model of rutile crystal, **b)** Electron diffraction pattern obtained from one grain **c)** Theoretical diffraction pattern from mono-crystalline rutile. The viewing angle in a) corresponds to the pattern in c).

4. Porosimetry

The pore volume respectively the pore area was measured using gas porosimetry (Figure 5). The peak of both the pore volume and area histograms are for pore diameters just larger than ten nanometers. From the porosimetry, the total pore volume and the total pore area can be obtained by integrating the histograms. We calculated the average pore diameter by assuming cylindrical pores with radius r and depth h, $2r = 4\pi r^2 h/2\pi rh = 4V/A$, where V is the total pore volume and A is the total pore area. This resulted in an average pore diameter of 10-13 nm.
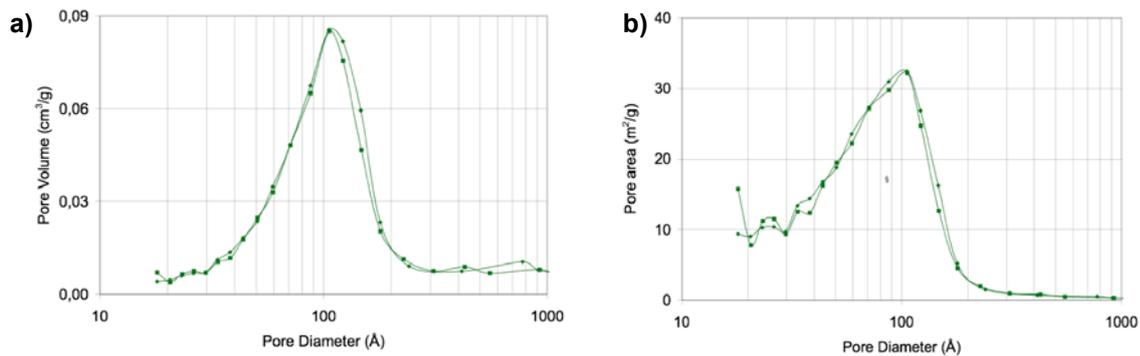
Figure 5 a) Pore volume as a function of pore diameter. **b**) Pore area as a function of pore diameter.

5. Discussions

The pore diameter can be estimated using a simple model. Assume that the coating grains are spheres, packed together as shown in Figure 6a. The pore diameter d can then be calculated according to Figure 6b and from the expression $d = (\sqrt{8} - 2)r \approx 0.83r$. For a sphere diameter of 20 nm the corresponding pore diameter will be 8 nm, and for a 30 nm sphere the pore will be 13 nm. Using this, we can compare the microscopy data with the porosity ones, and these two kinds of results agrees well with each other.

We can also estimate the total area in a coating. Suppose that a sphere of radius r is placed on every $(2r)^2$ square on the anode surface. The surface area of a sphere with radius r is $S = 4\pi r^2$, which means that the actual area is $4\pi r^2/4r^2 = \pi$ times larger than the flat surface. So for each layer of spheres the anode surface area increases by a factor of π. Since a typical coating is 10 μm thick it contains about 300 layers of spheres. This agrees with the other estimates [1] that the DSA® technique increases the total surface area between 10 and 1000 times depending on the number of layers in the coating. The surface area increase can therefore be explained by our coating grain hypothesis.
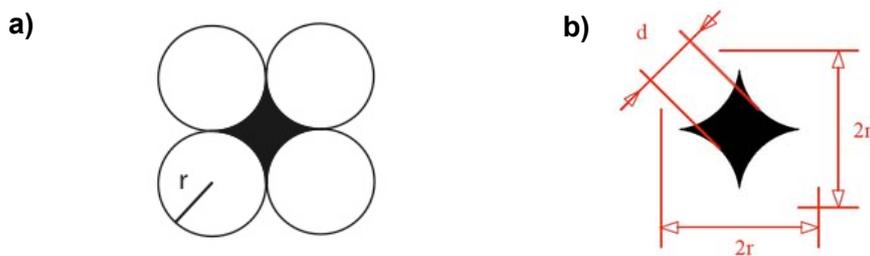
Figure 6 Schematic pictures of coating, spheres and pore models

The entire surface area estimated here is not necessarily catalytically active; instead this is an upper limit. The porosimetry done here, using N_2 gas, as well as our simple model above, give the total area. Complementary electrochemical studies such as by measuring both intensive and extensive quantities, where the intensive ones are independent on the surface area [3] are valuable.

High resolution microscopy of DSA® is limited, but we can compare our AFM measurements with the ones by Vallet [5], giving consistent results. Wang et al [7] has studied the microstructure of Ru/Sn based DSA® by TEM showing crystallites with a size of 30-100 nm depending on the preparation conditions, giving some support to our finding. However, it would be valuable to investigate the whole coating thickness in cross section by TEM.

6. Conclusions

Dimensionally stable anode (DSA®) coating consists of mono-crystalline grains of 20-30 nm size. The measured average pore diameters from microscopy and gas porosimetry agree well with each other. The findings support the common statement of a 10-1000 fold increase of surface area in DSA®, and suggest that the dominating source of surface enlargement is due to nanocrystallinity.

Acknowledgements

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