Nanocrystallinity in RuO$_2$ coatings—Influence of precursor and preparation temperature

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ABSTRACT

The effects of precursor and calcination temperature on the nano morphology of ruthenium dioxide on titanium, prepared from thermal decomposition of aqueous salt solutions were investigated. Transmission electron microscopy, X-ray diffraction, gas porosimetry and cyclic voltammetry showed that lower calcination temperature yielded smaller crystallites. The crystallites were between 6 and 22 nm in diameter. When using ruthenium nitrosyl nitrate the firing temperature had a large impact on the grain size, but for chloride there was only a minor effect in the temperature range 350–550 °C.

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1. Introduction

Ruthenium dioxide (RuO$_2$) is of both scientific and technological importance because of a combination of unique characteristics such as high thermal and chemical stability, low resistivity, and remarkable redox properties [1]. It has for example been used as the primary catalyst in production of chlorine and chlorate for over 40 years in the form of coating on titanium electrodes, so called Dimensionally Stable Anodes (DSA®). As shown in a previous study [2], RuO$_2$ synthesized by thermal decomposition of aqueous salt solutions crystallizes in rather uniform nanoscopic, monocrystalline grains. The superior electrocatalytical properties of so-prepared material were shown to be partly explained by the surface enlargement (in agreement with earlier estimates between 10 and 1000 times [3]) resulting from the spontaneous nanostructure. A way to control electrochemical properties is thus to learn how to control the nanoscopic grain structure, in the long run providing a route to lower energy consumption. RuO$_2$ has also been used in supercapacitors because of its high electrochemical reversibility [4]. The nanostructured architecture found in binary (Ru–Ti) O$_2 \cdot n$H$_2$O compositions favors the physical adsorption of water and maintains high water content [5].

The economical and simple method of thermal decomposition of an aqueous salt solution creates a film that is stable during gas evolution reactions in aggressive environments. Ruthenium nitrosyl nitrate (RuNO(NO$_3$)$_3$) is sometimes used as a precursor [6,7,9] instead of the more commonly used chloride salt (RuCl$_3$) for ruthenium oxide electrodes to avoid residual chlorine. Many studies of varying the preparation temperature [6–9] of ruthenium oxide electrodes and DSA® have been performed over the years. The voltammetric charge (q^*) decreases with increasing calcination temperature but the dependence curves have a complex shape [8,9].

Here we investigated the effect of two parameters, precursor and calcination temperature, on the grain sizes of RuO$_2$ coatings on titanium. The scope was to investigate the connection between the nano structure and the active area, combining different measurement techniques. We used transmission electron microscopy (TEM), X-ray diffraction (XRD) and gas porosimetry to measure the coating grains and the total area of the electrodes. The electrochemically active surface area was determined by cyclic voltammetry. We found that ruthenium dioxide coatings made from ruthenium nitrosyl nitrate, prepared at low temperature (350–400 °C) have small grains, large total area, and large voltammetric charge. Ruthenium dioxide prepared from ruthenium chloride calcinated in the temperature range 350–550 °C showed almost constant grain size, total area and voltammetric charge.

2. Experimental details

Commercially pure titanium plates, 0.5 mm thick, were degreased and etched in 1% hydrofluoric acid for 1 min. RuCl$_3$ and RuNO(NO$_3$)$_3$ were separately dissolved in water to a concentration of 38 g Ru/L

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solution. From these two stock solutions, three mixtures were prepared: 25% of chloride solution with 75% of nitrate solution, 50–50, and 75–25 (percentage per volume). Samples were prepared by applying the five solutions (stock and mixtures) to the titanium plates using a brush. The samples were dried in 90 °C for 10 min and fired in air for 10 min in temperatures from 350 °C to 550 °C, creating 25 different samples of RuO_2 electrodes. The samples were cut for characterization with different techniques. The film thickness was calculated from weight increase after calcination, assuming that all increase comes from pure RuO_2, and was approximately 0.5 μm on samples for TEM, XRD and cyclic voltammetry and between 2 and 2.5 μm on samples for porosimetry.

Imaging was done by a transmission electron microscope (JEOL 2000FX). The TEM samples were prepared by scraping off the coating using a sharp knife and collecting the powder on TEM grids (Carbon grid 200 mesh). X-ray diffraction was done with the grazing incidence technique on a Siemens D5000 diffractometer (Cu K_α, $\lambda = 1.5406$ Å). A Sol-X detector scanned between 24 and 60° in 2θ with an angle of incidence of 0.5°. The crystal size was calculated from the diffraction profile by the Scherrer equation [10].

Gas porosimetry and Bruanauer Emmet Teller (BET) measurements [11] were made using a Micromeritics, ASAP 2010 porosimeter. Nitrogen adsorption data was analyzed using the Barrett, Joyner and Halenda model [12]. Prior to measurements the samples were degassed at 100 °C.

The voltammetric charge was evaluated from cyclic voltammograms measured in deaerated 1 M NaOH at 25 °C. Circular electrode samples, 1 cm^2, were used. A platinum mesh served as the counter electrode and the reference electrode was a saturated calomel electrode (SCE) from Radiometer Copenhagen. The voltammograms were measured between −0.8 and +0.2 V vs. SCE with a sweep rate of 20 mV/s.

3. Results and discussion

TEM showed that our RuO_2 coating consisted of grains with a rather uniform size distribution. The grain size depends on, both, choice of precursor and calcination temperature. We found that RuO_2 prepared at low temperature had small coating grains (5–10 nm) and that RuO_2 prepared at high temperature had larger grains (20–30 nm). Some support of this can be found in the result of Roginskaya and Morozova [7] who observe 15–18 nm crystallites in mixed oxide specimens using TEM. They show that the crystallite size increases with preparation temperature but only for temperatures higher than 650 °C. It is difficult to get a representative quantitative estimate of the crystallite size using TEM, due to the limited sampling volume and therefore only images of typically large and typically small grains are presented (Fig. 1). XRD, being a volume-averaging technique, could provide more statistically accurate estimates.

From the X-ray diffractograms (Fig. 2a) the crystallite size in the sample can be estimated by the Scherrer equation: $L = K\lambda/(\beta \cos \theta)$ where L is the mean dimension of the crystallites in the sample, β is the width of the peak (at half maximum intensity) in the diffraction profile (measured in radians) and K a constant approximately equal to unity [10]. The estimation is valid under the assumption that all line broadening is due to finite crystallite sizes. As shown in Fig. 2b the crystallite size increases with increasing firing temperature. The trend was clearer for the RuO_2 samples prepared from ruthenium nitrosyl nitrate, with a fourfold increase of crystallite size while for the RuO_2 samples prepared from ruthenium chloride the trend was less profound. Roginskaya and Morozova [7] studied only mixed oxide electrodes prepared from chloride and so far our result is in good agreement. Nitrosyl nitrate decomposes at a lower temperature than chloride [6] and could be the reason why the temperature dependence on crystallite size is effective at a lower temperature.

Using XRD, a growth of titanium oxide was found in all samples calcined at 550 °C and in samples prepared from chloride calcined
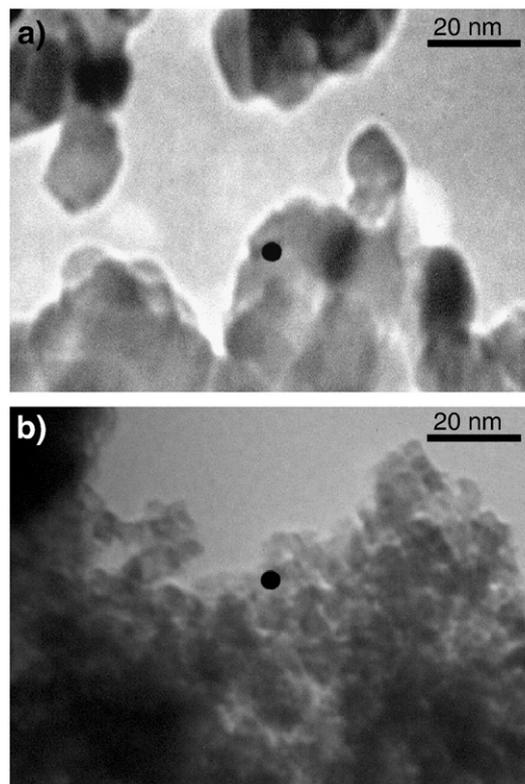

Fig. 1. TEM images of ruthenium dioxide grains. The grain size depends on both precursor and calcination temperature but a quantitative measurement is hard to do from these images. a) Large grains (100% nitrosyl nitrate fired at 550 °C) and b) small grains (100% nitrosyl nitrate fired at 350 °C).

at 450 °C and above. The titanium dioxide (TiO_2) signal was generally very weak compared to the RuO_2 signal, with the exception of the "chloride 550 °C" sample (Fig. 2c). It showed clearly a double peak at approximately $2\theta = 27$ °, representing the rutile phase of titanium and ruthenium dioxide, respectively, and a small titanium dioxide anatase peak at $2\theta = 25$ °. Since in this case the coating consists of pure RuO_2 the only available source of titanium is the substrate. When instead using mixed oxides of ruthenium and titanium the same double rutile peak sometimes occur in the X-ray diffractograms, as a result of phase separation during firing. This has been observed by Chang and Hu [5] and suggests that ruthenium not always replaces the titanium atoms in the rutile structure as is earlier reported [3].
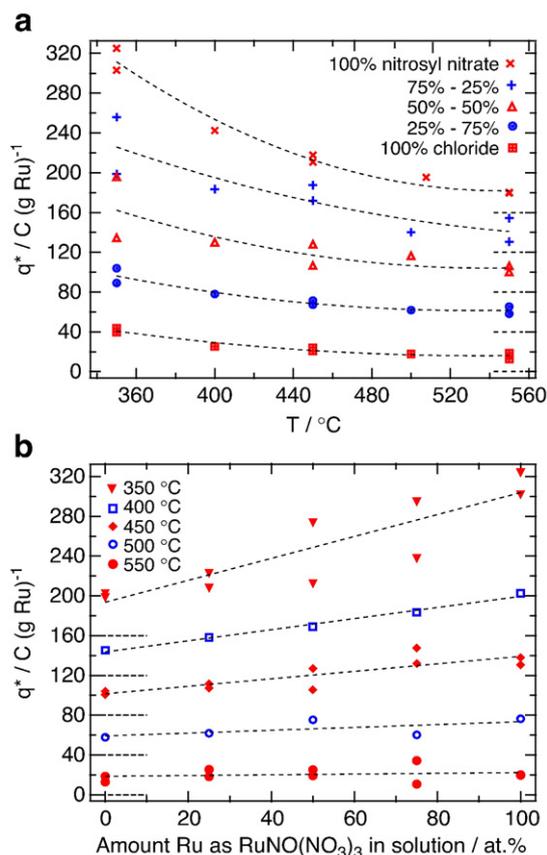
The voltammetric charge decreased with increasing calcination temperature (Fig. 3), consistent with earlier reports [6,7]. It was also lower for electrodes prepared from chloride than for electrodes prepared from nitrosyl nitrate, which agrees with the findings of Fachinotti et al. [8], but the precursor dependence decreased with increasing temperature. At low temperatures the precursor had a large impact on the voltammetric charge; more nitrosyl nitrate gave a higher voltammetric charge. At high temperatures there was almost no precursor dependence at all. Since the voltammetric charge is proportional to the active area of the electrode [13], and the grain size has a direct influence on the total area, a sample with small grains and large total area would have a larger active area and therefore higher voltammetric charge. In contrast to the simple temperature dependence we see with all our experimental techniques, it should be noted that Fachinotti et al. [8] and Ardizzone et al. [9] report on complex temperature dependence.

The pore volume and the pore area were measured using gas porosimetry. From the porosimetry, the BET surface area can be obtained. The BET surface area measurement gave an approximate value of the total surface area of the sample; measured per gram of coating, see Table 1. In contrast to voltammetric charge measurements, gas
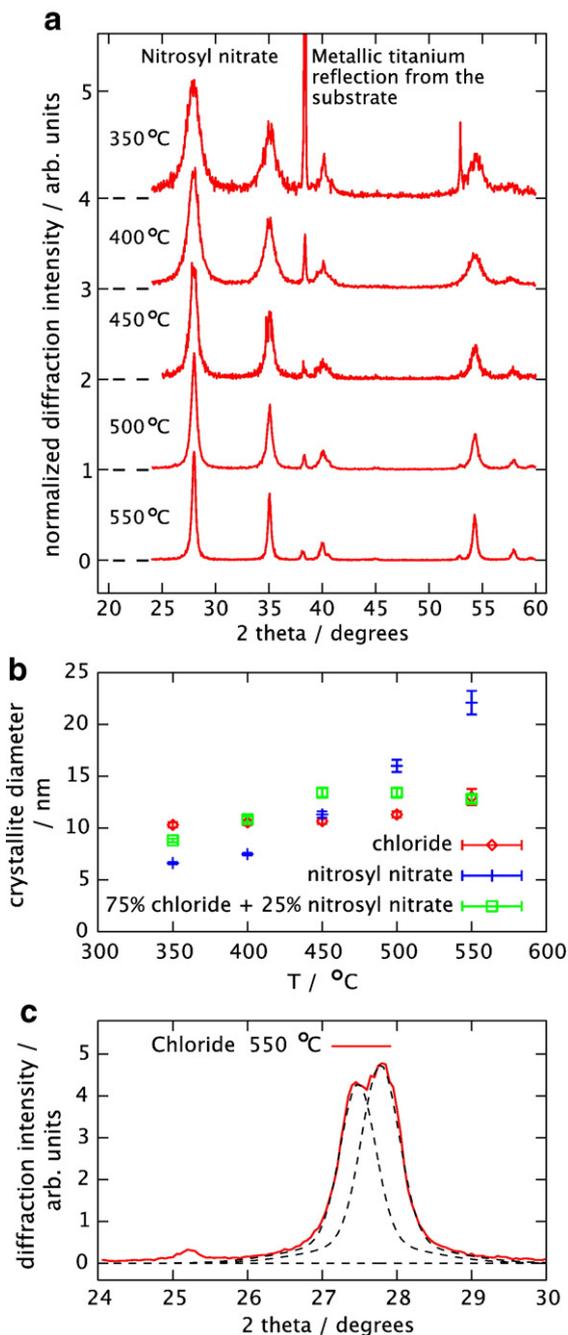
Fig. 2. a) Measured diffraction patterns, illustrating the varying peak width. Curves are offset and normalized on first peak height for clarity. b) The crystallite size in the sample calculated from the breadth of the diffraction peak, using the Scherrer equation. c) The growth of titanium oxide during firing is visible in the ruthenium dioxide prepared from chloride and calcinated at 550 °C, as a double peak at $2\theta = 27°$, representing the rutile phase of titanium and ruthenium dioxide, respectively, and at the titanium dioxide anatase phase peak at $2\theta = 25°$.

Fig. 3. Voltammetric charge for a) different calcination temperatures and b) different precursor mixtures. Curves are offset as indicated for clarity.

(7050 kg/m³) and A_{BET} is the BET surface area (total area per unit mass). The so-estimated grain sizes are shown in Fig. 4, together with the crystallite sizes estimated from XRD measurements. As can be seen, the XRD and BET agree qualitatively in the sense that samples prepared from RuCl₃ display grain sizes almost independent of preparation temperature, while RuNO(NO₃)₃ yields highly temperature dependent grain diameters. (This is further in qualitative agreement with the voltammetric charge in Fig. 3a). However, quantitatively, there is about a one order-of-magnitude discrepancy between the sizes estimated from porosimetry and diffraction data. The explanation is most likely that the crystallite grains are not loosely packed. They are rather sintered or clustered together in such a way that only a fraction of the boundary surface of the crystallites is accessible for the gaseous probe of the porosimetry. An additional, interesting discrepancy is that the temperature trends of the grain sizes determined from XRD or porosimetry have a crossing somewhere between the highest and the lowest temperature (*i.e.* at low *T*, chloride results in larger diameters than nitrosyl nitrate, but at high *T* this is reversed). This cannot be observed in the voltammetry data in Fig. 3, where the high temperature yields the smallest active surface independent of precursor. This means that gas porosimetry and cyclic voltammetry do not probe exactly the same surface.

porosimetry estimates the entire area, which is not necessarily catalytically active. The catalytic active area, on the other hand, is not the whole answer to the catalysis efficiency; the grain shape for example determines the selectivity of the catalysis [14]. This means that the oxide with the largest catalytic surface area not necessarily makes the most efficient electrode. From BET surface area measurement the mean diameter of the grains can be estimated under the assumption that the coating consists of loosely packed spherical grains with uniform size distribution, the diameter of a grain can be expressed as $d_{grain} = \frac{6}{\rho_{RuO_2} A_{BET}}$ were ρ_{RuO_2} is the density of ruthenium dioxide

Table 1
BET surface area results.

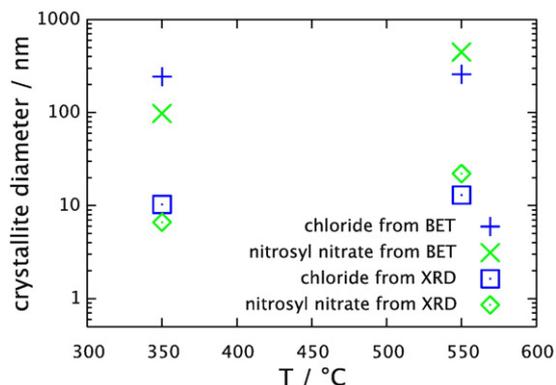|	Nitrosyl nitrate	Chloride
350 °C	8.7 m²/g	3.5 m²/g
550 °C	1.9 m²/g	3.3 m²/g

Fig. 4. Crystallite size estimated from XRD measurement and grain size calculated from BET surface area measurement.

4. Conclusions

We have studied the effect of precursor and calcination temperature on ruthenium dioxide electrodes prepared from thermal decomposition of aqueous ruthenium salt solutions. All four measurement techniques, (TEM, XRD, q^* and BET surface area) gave qualitatively consistent results. Ruthenium nitrosyl nitrate, calcinated at a low temperature (350–400 °C) resulted in ruthenium dioxide particles that were rather small (5–10 nm). Because of the small particles in the coating, such an electrode had a large total area and high voltammetric charge. The same precursor calcinated at a high temperature (500–550 °C) showed instead an opposite trend with large particles (20–30 nm), small total area, and low voltammetric charge. Ruthenium chloride calcinated at any temperature in the range of 350–550 °C showed ruthenium dioxide particles of about 12 nm, which is

similar to that of ruthenium nitrosyl nitrate calcinated at 450 °C. Some sort of clustering of the crystallites occur in the preparation process, giving BET surface areas that are unexpectedly low compared to the grain sizes. The active area is for both precursors lowest for the highest calcination temperature while the grain size only grows with the temperature for oxide prepared from nitrosyl nitrate and does not grow at all for oxide prepared from chloride.

Acknowledgements

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