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LETTER

Synthesis of nanosized Zn_2PtO_4

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Platinum and platinum compounds are used in numerous catalysis applications. In the fuel cell field, platinum is the main choice of catalyst material. Platinum forms a significant cost of the fuel cell system, and lots of research effort strives to decrease the platinum amount while preserving the efficiency of the catalyst material. This can be achieved in a number of ways, such as decreasing the particle size of the platinum particles, or by using more efficient platinum alloys. However, recent studies have shown that the platinum catalyst is subject to degradation in the relatively harsh fuel cell environment [1], and smaller particles become more sensitive to degradation due to their higher specific surface area. Platinum alloys, such as Pt–Ru, have shown to be more efficient catalysts, and to be less sensitive to catalyst poisoning, compared to pure platinum [2, 3]. Catalyst poisoning can occur in for example direct methanol fuel cells (DMFC) when methanol leaks through the polymer electrolyte membrane and reaches the cathode side [4], or on the anode side, when methanol is oxidized to CO. The main disadvantage with the platinum alloys though, is that they degrade more rapidly than pure platinum in a fuel cell.

In the search for more stable alternatives to platinum and platinum alloys, platinum oxides is a relatively unexplored field. In theory, platinum oxides may be more resistant to degradation as they are already in the oxidized state. On the anode side of a DMFC, oxides such as $PtRuVO_x$ and $PtRuWO_x$ were reported to be very efficient and resistant to CO oxidation compared to pure platinum [5]. For the oxygen reduction reaction on the cathode side, oxides such as Sr_3NiPtO_6 and $Bi_2Pt_{2-Y}Ir_YO_7$ have been reported to have good performance [6, 7]. We recently reported, however, that for Sr_3NiPtO_6 and Sr_3CuPtO_6 this is due to a decomposition of the oxides to elemental platinum, thus showing that the stability of these oxides is not sufficient for a fuel cell application. Therefore, focus should be put on electrochemically more stable metal oxides [8].

Since platinum is a material of high chemical resistance, the conditions involved in the synthesis of platinum oxides are generally harsh, such as alkali melts [9], electrosynthesis [10] or high oxygen pressures [11, 12]. These synthesis methods generally produce large crystals with a low surface area, excellent for structure determination in single crystal X-ray diffractometry, but less suitable for catalytic applications where a high surface area is desirable.

Zn_2PtO_4 and the isostructural compound Mg_2PtO_4 were first synthesized by Muller and Roy [13] and were reported to have an excellent chemical resistance. The oxides have an inverse spinel structure. The synthesis conditions involved were quite harsh, with oxygen pressures of 150–200 bar and temperatures around 900 °C.

Synthesis of Zn_2PtO_4 at such high oxygen pressure and temperature proceeds as

$$Pt + 2Zn(OH)_2 + O_2 \rightarrow Zn_2PtO_4 + 2H_2O$$

where Pt is oxidized to Pt^{4+} by oxygen.

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Here we report a new facile metathetical preparation of nanosized Zn_2PtO_4. In a metathetical reaction method the oxidation state of platinum remains unchanged, according to:

$$PtCl_4 + 4ZnO \rightarrow Zn_2PtO_4 + 2ZnCl_2$$

The excess $ZnCl_2$ may be easily removed by washing with water. A similar synthesis method has previously been used to synthesize $PtCoO_2$ and $PdCoO_2$ [14, 15].

The sample preparation was done in a glovebox with an inert argon atmosphere. In a typical experiment, 0.34 g of $PtCl_4$ (99.9+%, Aldrich) was mixed with 1.3 g ZnO (nanopowder, specific surface area 15–25 m^2/g, Aldrich), or 0.64 g MgO (nanopowder, specific surface area 130 m^2/g, Aldrich). The molar ratio of $PtCl_4$ versus ZnO (and MgO) was thus 1:16. The ZnO (or MgO) powder was dried at 120 °C for 12 h prior to use. The chemicals were dispersed in 5 mL of CCl_4 (99.9%, Aldrich) and ground thoroughly in a mortar. The CCl_4 was allowed to evaporate and the mixture was put in a sealed quartz tube with an argon atmosphere. The quartz tube was put in a tube furnace with an N_2 atmosphere at 500 °C for 72 h. The product was washed with 10 wt% of HCl in order to remove unreacted ZnO and formed $ZnCl_2$, and then washed repeatedly with deionized water and dried in air at 120 °C. The product was further purified with gravimetric separation to remove platinum formed as a by-product. This was done by mixing the powder with deionized water in a 1:10 volumetric ratio and subjecting the mixture to ultrasonic treatment for 10 min. The water dispersed powder was then placed in a petri dish on a horizontal shaking table for 12 h. This treatment separated the black platinum powder from the yellow Zn_2PtO_4 crystals due to the large differences in density between the two phases. The Zn_2PtO_4 crystals were collected and dried in air at 120 °C. Powder XRD was performed with a Siemens D5000 diffractometer with CuKα radiation. Transmission electron microscopy (TEM) was done with a JEOL JEM-1200 EX II operating at 120 KV. The samples to be analysed by TEM were dispersed in ethanol, and sonicated in an ultrasound bath for 5 min. One drop of the dispersion was placed on top of a copper supported holey carbon grid and allowed to evaporate.

A number of different synthesis temperatures were evaluated. Shown in Fig. 1a is a powder diffractogram of a sample obtained at 650 °C. As seen in this diffractogram, platinum is the main constituent in this sample, giving rise to the peaks at 39.76 (1 1 1) and 46.25 (2 0 0). Zn_2PtO_4 was a minor component in this sample. The amount of free platinum decreased with the synthesis temperature, and an optimum temperature was found at 500 °C. No reaction occurred at 450 °C and below. Figure 1b shows the XRD diffractogram for the product obtained at 500 °C. As seen from the figure, there was still a small amount of elemental platinum present in the sample. Attempts to dissolve the

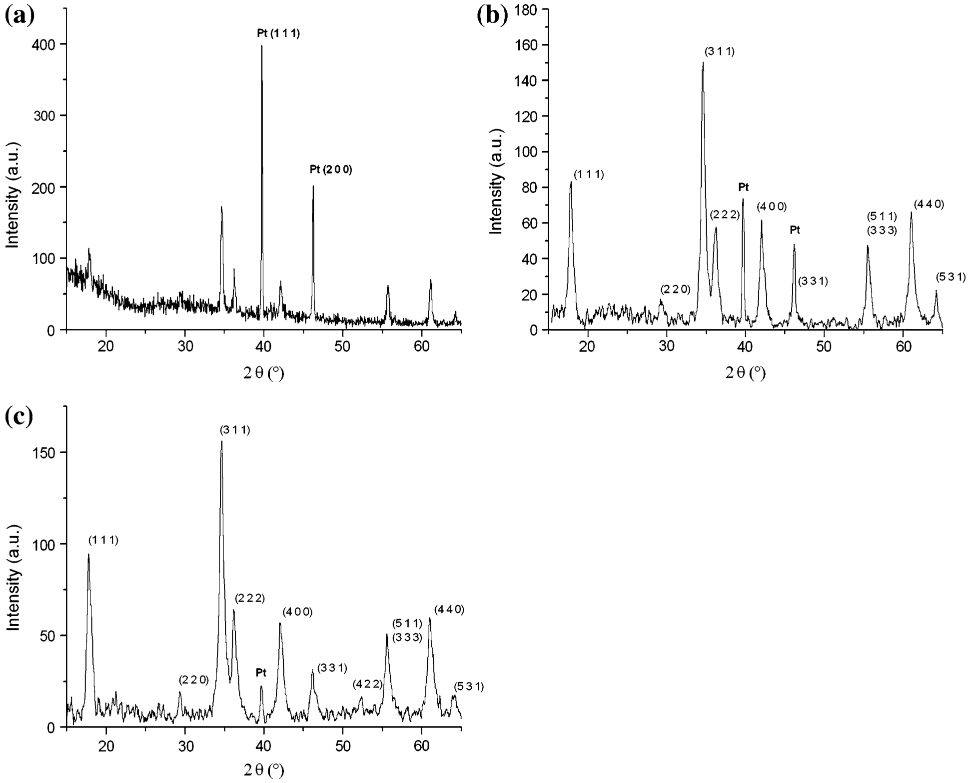

Fig. 1 Powder XRD diffractogram of the product obtained from synthesis at **a** 650 °C and **b** 500 °C, unpurified, **c** 500 °C, purified. Peaks arising from platinum residue can be seen at 39.76 (1 1 1) and at 46.25 (2 0 0)

platinum in Aqua regia successfully removed the platinum, but also dissolved a large fraction of the Zn_2PtO_4. According to literature, Zn_2PtO_4 should be stable in Aqua regia [13], but that was reported for a material that was prepared using a synthesis method that produced much larger grain sizes than the ones obtained here. Evidently the smaller crystals of Zn_2PtO_4 prepared here dissolve in Aqua regia to a higher extent than larger crystals do. With the gravimetric technique described previously, the platinum content was decreased even further, as shown in Fig. 1c. A few attempts were also done to try to synthesize Mg_2PtO_4, using the same $MgO:PtCl_4$ ratios as for $ZnO:PtCl_4$, and within the same temperature range. This failed to produce any Mg_2PtO_4, and the reason is probably the less favourable enthalpies of formation for this reaction.

The broad peaks seen in the diffractogram in Fig. 1c indicates a small crystal size. A bright field TEM image of the Zn_2PtO_4 crystals is shown in Fig. 2. As seen from this figure, the crystals are spheroidal to cubic, with no sharp crystal facets. The size of the crystals is around 10–30 nm. From the Williamson-Hall plot in Fig. 3, we can calculate an average crystal size to 26 ± 2 nm. Conclusively, the average crystal size is in the same size range as the crystals of the ZnO precursor used in the synthesis. Thus, it seems likely that the crystal size of the Zn_2PtO_4 powder depends on the crystal size of the ZnO precursor. This will be the subject of future studies.

In summary, a new method has been developed for the synthesis of nanosized Zn_2PtO_4. The method enables the synthesis of Zn_2PtO_4 at a relatively low temperature (500 °C) and at ambient pressure. The use of a low temperature creates a powder with a small particle size, making it suitable for the use in catalyst preparations. This is a significant advantage compared to earlier methods that require high temperatures and oxygen pressures and produce low-surface area samples.

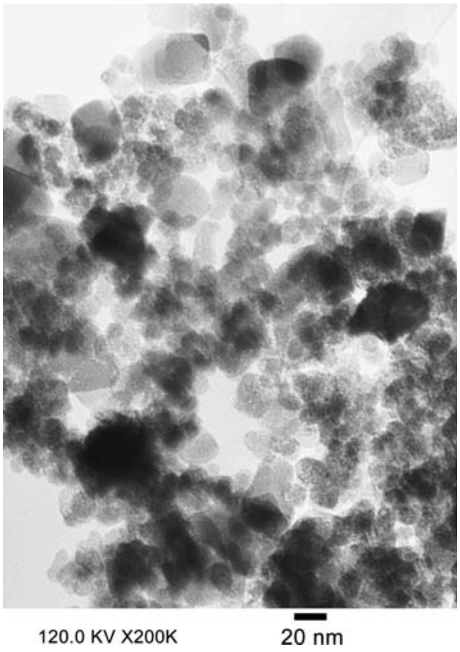

Fig. 2 TEM image of the Zn_2PtO_4 nanopowder. Scale bar = 20 nm

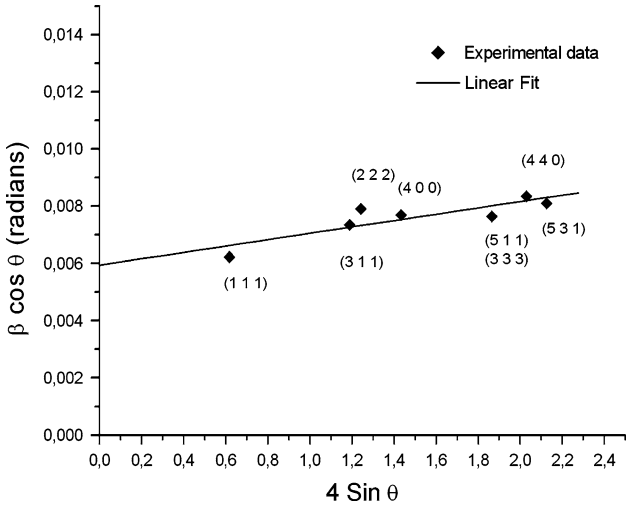

Fig. 3 Williamson-Hall plot of the reflections. (◆) = experimental data, (–) = linear fit

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