

Supporting information

Crystallization route for preparation of Ta- and Nb-doped titania

The doping of tantalum into titania was achieved by using TiCl_4 and TaCl_5 as precursors. Both TiCl_4 and TaCl_5 were dissolved in anhydrous methanol in an argon atmosphere; these solutions are air-stable. After combining the solutions, ammonia was added which resulted in the formation of titanium and tantalum alkoxides, namely $\text{Ti}(\text{OCH}_3)_4$ and $\text{Ta}(\text{OCH}_3)_5$. These were flash calcined at 1050°C to produce tantalum-doped titania. Powder X-ray diffraction (PXRD) phase analysis shows that the Ta-doped rutile product is quite pure, with only a very small amount of residual Ta_2O_5 . Electron probe microanalysis (EPMA) confirms that the sample was fully reacted thereby comprising a single phase material, and is homogeneous in composition (i.e. homogeneous in Ti:Ta ratio). There is evidence for some minor chemical variation within individual grains. Quantitative EPMA studies of the Ti:Ta ratio from 40 sample points in multiple grains gave an average chemical formula of $\text{Ti}_{0.94}\text{Ta}_{0.06}\text{O}_2$. The synthesis method is relatively simple and produce a well-doped pure material with $> 95\%$ recovery.

An attempt was made to produce Nb-doped titania (100g) using TiCl_4 and NbCl_5 following the same method reported above for producing tantalum doped titanium dioxide. However, PXRD phase analysis shows that the product consisted of a mixture of two phases — Nb-doped rutile (92%) and TiNb_2O_7 (8%). At least 80% of the niobium resides in the non-conducting TiNb_2O_7 phase. Conversion of the TiNb_2O_7 phase into a conducting rutile phase was attempted but abandoned due to lack of success. An alternative method was trialled using K_2TiF_6 and K_2NbF_7 salts as precursors. These two salts are dissolved in excess concentrated sulphuric acid and the solution is heated with the addition of perchloric acid to evaporate HF. After the addition of ammonium chloride, ammonia is used to neutralise the excess acid and a precipitate forms. After filtration and washing with 2% NH_4NO_3 and water, the solid is calcined at 1050°C to form an Nb-doped titania product. However, scale-up of this method was limited by (i) the need for an HF fuming step and (ii) product contamination with potassium niobate.

Initial Measurements on Ta-doped Titania

Ta-doped TiO₂ feedstocks were prepared in-house from their metal chloride precursors. PXRD, SEM and electron microprobe analyses revealed that the tantalum-doped material was homogeneous and pure. The prepared bars are composed of generally fine-grained material (< 20-30 μm) that has been sintered together to produce coarser composite grains. The presence of light and dark grains in the SEM studies indicate slight variation in composition between individual grains i.e. slight variation in Ta:Ti ratio between grains. There is no evidence for unreacted starting material or the development of other Ta-Ti-O phases. Quantitative analysis of the Ti:Ta ratio from 40 sample points in multiple grains gave an average chemical formula of Ti_{0.94}Ta_{0.06}O₂.

In initial tests, the cell voltages were quite high for two electrolysis runs using duplicate sample bars. This high cell voltage (> 9 V) was mostly attributed to poor conductivity. In order to improve the conductivity, a sample of Ta-doped TiO₂ was sintered at 1100°C in a nitrogen atmosphere with very low oxygen levels during electrode fabrication. Two experimental tests on material prepared in this manner gave even higher cell voltages (11-12 V). There was some indication from high resolution back scattered SEM images that the texture exhibited by several shards of Ta-doped TiO₂ material were suggestive of a glassy phase. At this point, it was clear that optimization of the Ta-doped titania materials was not straightforward. Results obtained with Nb-doped titania (a less costly material) appeared more promising and were pursued as an alternative.