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Preparation and high-temperature characterisation of nanostructured alumina ceramic membranes for gas purification

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Abstract

Porous anodic alumina discs supporting palladium films as elements of hydrogen-purifying membranes have been examined for their high-temperature behaviour. The method employed to fabricate the porous alumina support is the so-called 'hard anodising' technique, which offers substantially higher growth rates while producing mechanically robust films. These alumina membranes were found to possess a thermal stability better than commercial Anopore® membranes. Upon long-term exposure at 800 °C they transform into γ-alumina without major deformation. Ultra-thin palladium films deposited across the alumina pores by physical vapour deposition are continuous and stable in reducing atmospheres to at least 700 °C but are oxidised and destroyed by heating in air.

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Keywords: Porous anodic alumina; Membrane fabrication; Thermal analysis; Palladium film

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1. Introduction

Hydrogen is an environmentally friendly energy carrier which is the focus of much current research and development. Many applications such as polymer electrolyte membrane fuel cells require high purity hydrogen. The separation of hydrogen from hot synthesis gas streams is therefore a key capability. The use of porous ceramic–palladium compound membranes offers a promising solution. Porous anodic alumina (PAA) with its straight, parallel and uniformly sized pores is an attractive support structure [1,2]. The conventional 'mild anodising' (MA) fabrication process for PAA membranes has a slow growth rate of only a few micrometers per hour. The use of 'hard anodising' (HA) as described by Lee et al. [3] accelerates the oxide growth to about 100 μm h^{-1}.

In this paper, we examine the high-temperature properties of PAA membranes prepared via HA in oxalic acid and compare them to membranes both commercially available and laboratory made by MA in sulfuric acid. We then describe deposition of an ultra-thin palladium film onto an MA PAA membrane and investigate its thermal evolution.

2. Experimental

PAA membranes were prepared by anodising one face of an Al foil (Alfa Aesar, 99.99%, 0.25 mm thickness, degreased). The setup, incorporating a thermostat and stirring for temperature control, is described by Lee et al. [3]. HA in 0.3 mol dm^{-3} oxalic acid was carried out at a voltage of 150 V versus a Pt cathode at 4 °C [3]. Within 4 h the oxide had grown to a thickness of 235 μm. MA in 0.3 mol dm^{-3} sulfuric acid was undertaken at 25 V and 7 °C as reported elsewhere [4]. The MA process is much slower and the oxide thickness reached only 175 μm after 24 h anodising. The remaining Al metal was removed by etching in a saturated iodine–methanol solution at 50 °C and the membranes were rinsed in methanol to clean off excess iodine. For comparison, commercial Whatman Anopore® membranes (13 mm diam., 60 μm thick, 0.2 μm

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pores), prepared in phosphoric acid, have been included in our analysis.

Thermal analysis combining differential scanning calorimetry (DSC) and thermogravimetry (TG) was carried out using an Alphatech SDT Q600 instrument. Powdered samples (20 mg) were heated in flowing nitrogen at 20 °C min^{-1}. Individual membranes were heated in a muffle furnace under ambient atmosphere to 800 °C. The heating and cooling rates were 10 °C min^{-1} and the dwell time 1 h. X-ray diffraction (XRD) was undertaken using a Philips PW1700 diffractometer with Co Kα radiation.

Prior to palladium deposition the pores of PAA membranes prepared by MA in sulfuric acid were opened and widened by etching in 5% H_3PO_4 for 60 min at 30 °C. Metal was evaporated onto the basal side (the Al metal contact side) of the alumina substrates using a Balzers BA510 coating system at a vacuum of 2×10^{-5} Torr or better. The metal source was arranged at 45° to the rotating substrate at 150 mm distance. Film thickness was monitored using a quartz microbalance. In a first step an intermediate layer of 40 Å Ti was evaporated using an electron gun, improving bonding of the palladium metal film. Subsequently palladium was deposited from an electrically heated alumina coated tungsten boat, typically at a rate of 25 Å s^{-1}.

The membranes were characterised using a JEOL 6500F FESEM. Grazing incidence XRD spectra were obtained for specimens heated in both ambient atmosphere and forming gas (5% H_2 in N_2) using a heating rate of 10 °C min^{-1} and a 1 h dwell time.

3. Results and discussion

3.1. Thermal analysis of hard anodized membranes

The result of combined thermal analysis on PAA prepared via HA in oxalic acid is shown in Fig. 1. The DSC trace shows two distinct exothermic events. The first is a very sharp peak centred around 912 °C, the second a broader and less intense peak centred at 1210 °C. The DSC trace shows the same features as measurements on ‘mild anodised’ specimens [5–7] permitting comparable interpretation. The first exotherm represents crystallisation of amorphous alumina into a transition alumina phase while the second event marks the transition to stable α-alumina.

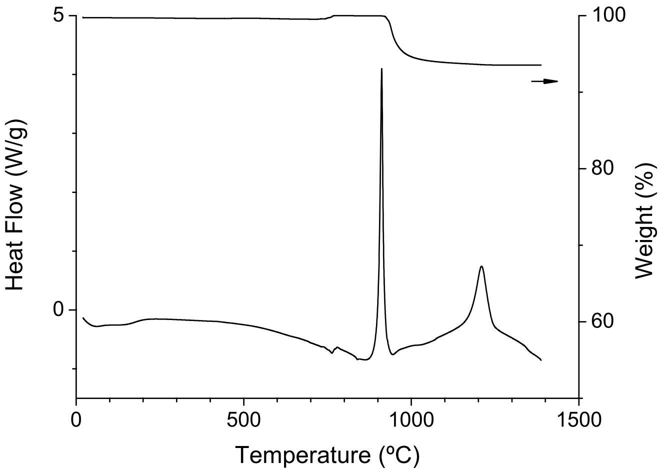

Fig. 1. DSC (left scale) and TG (right scale) analysis of PAA prepared by HA in oxalic acid.

Due to the dynamic nature of this experiment the results are best compared to data obtained at the same heating rate of 20 °C min^{-1}. The temperature of the first exotherm marks the initial occurrence of a crystalline alumina phase, 850 °C for the Anopore® membrane but 970 °C for membranes prepared by MA in sulfuric acid [8]. While precise temperature values will not apply to quasi-static heating they yield the information that Anopore® membranes crystallise at the lowest temperature, followed by membranes prepared in oxalic acid. Membranes fabricated in sulfuric acid show the highest transition temperatures. This is demonstrated by heating individual membranes of various types up to 800 °C. The respective XRD traces are shown in Fig. 2.

While the anodic alumina prepared using sulfuric acid was still amorphous the two others showed clear evidence of crystalline phase formation. For HA in oxalic acid this was γ-alumina and for the Anopore® membrane θ-alumina. As previously reported the Anopore® membrane curled up at 800 °C [8] whereas the HA (oxalic) and MA (sulfuric) membranes showed little or no planar distortion.

The TG trace in Fig. 1 shows a weight loss of 6.5% for anodic alumina prepared by HA in oxalic acid heated up to 1400 °C. The majority of this loss occurs within 100 °C after the onset of the first crystallisation. Lee et al. [3] report impurity contents of 1.8 wt% carbon and only 0.1 wt% water. The almost complete loss of these species (with the carbon as CO_2) matches the observed weight loss.

3.2. Deposition and thermal evolution of a Pd layer

Deposition of Pd metal vapour onto the very smooth basal face resulted in a highly uniform film of 150 nm

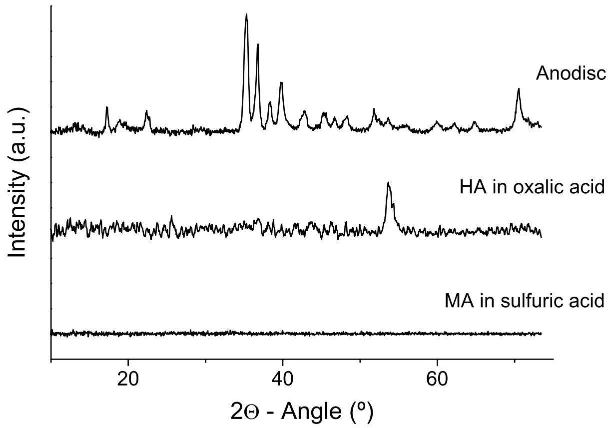

Fig. 2. XRD of anodic alumina membranes heated to 800 °C (Co Kα radiation).