Conformal coating of nanoscale features of microporous Anodisc[TM] membranes with zirconium and titanium oxides†

Piyush Shukla,[a] Edel M. Minogue,[a] T. Mark McCleskey,[a] Q. X. Jia,[b] Yuan Lin,[b] Ping Lu[c] and Anthony K. Burrell*[a]

We have successfully coated a nanofeatured material with ZrO_2 and TiO_2 using a polymer assisted deposition technique.

Coating porous materials remains a major challenge because many of the techniques used to deposit high quality films involve line-of-site techniques such as physical vapour deposition or chemical vapour deposition. The nature of these techniques makes it almost impossible to coat materials that have nanoscale porous features. The ability to coat such surfaces will become more and more important as nanotechnology progresses and complex hierarchical structures are prepared. The two main requirements for coating nanofeatured materials are good penetration into the features and a conformal coating that matches the surface structure so that the nanofeature is not closed-off or filled-in. Conformal coating is also a growing requirement of the electronics industry, which continues to reduce the size of features on advanced microchips. We report here on a new solution technique known as Polymer Assisted Deposition[1] (PAD) and its ability to coat porous materials with 200 nm openings.

We chose the challenging yet well-defined substrate of Anodisc[TM] membranes. These alumina discs have well-defined straight channels of 200 nm that traverse the entire thickness of the membrane (60–100 µm). Previous work on coating these membranes with gold[2] and other metal oxides (including TiO_2, MnO_2, V_2O_5, Co_3O_3, ZnO, WO_3 and SiO_2)[3,4] highlighted the issues associated with conformally coating nanofeatured materials. Classical sputtering of gold leads primarily to the coating of the top surface layer, as predicted. A 70 nm layer can be deposited on top of the membrane surface which leads to a narrowing of the pore size down to <7 nm, but the gold does not penetrate deeply down the channels. Gold has also been deposited by a solution-based electrochemical method that resulted in coating the membrane primarily at the surface, leading to substantial necking at the pores. The narrow opening has been used as a molecular gate for separation applications. This method, however, can only be used to coat a very limited number of film types. The sol–gel technique, when used to coat Anodisc[TM] membranes, led to the formation of metal oxide nanostructures. However, these structures closed-off the pores of the membrane.[3,4] Supercritical CO_2 has also shown success in depositing conformal coatings, however it has been limited to a few select metals and non-porous materials.[5]

Anodisc[TM] membranes are very stable at neutral pH, but the alumina structure begins to degrade at pH > 9.5 and pH < 3.5. Zirconium and titanium are known to show extremely high corrosion resistance, brought about by the formation of an oxide film on the surface, in a broad range of aqueous environments. Zirconium oxide has long been used as a protective layer against degradation, more recently, for example, in automobiles[6] and in other applications such as catalysis, e.g., for the isomerization of alkenes,[7] and in optics for smart thermo-[8] or electro-[9] optical modulation. Titanium oxide is common in the aerospace, chemical and electrochemical industries, as well as being widely used in metallic biomaterials.[10–12] We report herein on the conformal coating of Anodiscs[TM] with zirconium and titanium oxides. The coatings are highly uniform and do not block the pores, suggesting a highly conformal coating. The zirconium oxide is shown to significantly enhance the corrosion resistance of Anodiscs[TM] in caustic media.

The chemical deposition PAD technique has been reported-on previously,[1,13] and is a variant of the traditional chemical solution deposition process. In PAD, a polymer is used to bind and solubilize the metal precursor in an aqueous solution. The polymer both increases viscosity and protects the metal, thereby preventing unwanted polymeric metal oxide formation prior to removal of the solvent. All of the Anodiscs[TM] had 200 nm pore sizes with a well-defined honeycomb pore structure, as seen in Fig. 1a, and a pore density of 4×10^{13} pores m^{-2}.[14] Four types of membrane were prepared:‡ (i) TiO_2-coated membranes from a 211 mM Ti solution, (ii) ZrO_2-coated membranes from a 250 mM Zr solution, (iii) ZrO_2-coated membranes from a 480 mM Zr solution and (iv) ZrO_2-coated membranes with two sequential coats from a

[a] Los Alamos National Laboratory, Chemistry Division, MS J514, Los Alamos, NM, 87545, USA. E-mail: burrell@lanl.gov; Fax: (+1) 505 665 9905; Tel: (+1) 505 667 3588
[b] Los Alamos National Laboratory, Materials Science and Technology Division, MS K763, Los Alamos, NM, 87545, USA
[c] Department of Materials Science and Engineering, New Mexico Institute of Mining and Technology, Socorro, NM, 87801, USA
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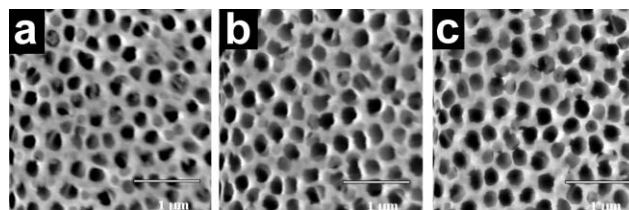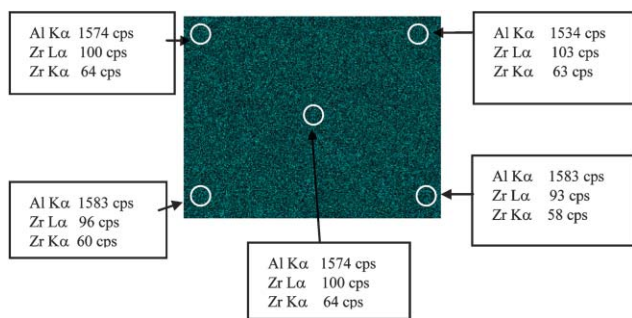
Fig. 1 (a) The well-defined honeycomb pore structure of an uncoated Anodisc[TM] with 200 nm pore sizes. (b) (250 mM; 1 coat) ZrO_2-coated Anodiscs[TM]. (c) (211 mM; 1 coat) TiO_2-coated Anodiscs[TM].

480 mM Zr solution. SEM observations and EDS analysis indicate the presence of very uniform, conformal ZrO_2 or TiO_2 coatings on the porous Al_2O_3 structure. The layer thickness of the singly-coated membrane (from the 250 mM Zr solution), determined by ellipsometry, is about 20 nm. The porous structure of the Al_2O_3 remains after the coating, with no Al_2O_3 pores appearing to be filled-up by the ZrO_2 or TiO_2 within the resolution of the SEM (Fig. 1).
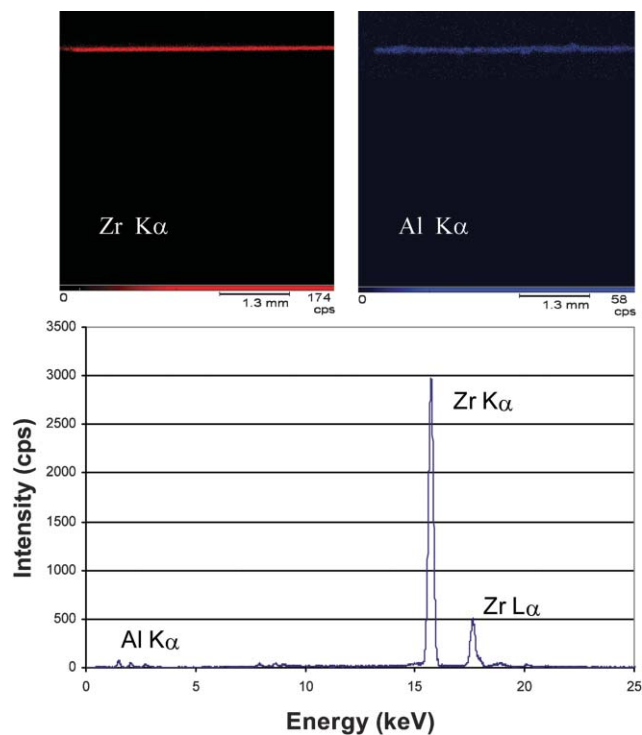
Imaging by MXRF (Fig. 2) shows that the coatings are highly uniform across the surface of the membrane. Across a 1.5 × 2 mm area, five different spots were randomly chosen for analysis. For the Ti-coated membrane, the Ti-K_α line had an average intensity of 59 cps with a standard deviation of 4 cps. For the Zr-coated membranes, the Zr-L_α line had an average intensity of 99 cps with a standard deviation of 4 cps for coatings from the 250 mm solution coating, and 163 cps with a standard deviation of 5 cps for the coatings from the 480 mM solution. These low standard deviations, ranging from 3 to 6%, demonstrate a highly uniform coating across the surface of the membrane. The coatings also appear to be uniform throughout the thickness of the membrane. The Zr-K_α, Zr-L_α and Al-K_α energy lines were observed (Fig. 3). An intensity ratio of 1 : 30, Al-K_α : Zr-K_α is observed. Fig. 4 shows the depth profile of the Zr-K_α intensities over the area at 50 μm-interval steps. The area scans show a homogenous deposition of Zr, both on the surface and inside the membrane. (Note: the drops in intensity across the scan at 50 μm and 100 μm are as a result of a bend in the membrane).

While the material is still porous, the coated Anodiscs[TM] are more stable to caustic conditions. The uncoated and ZrO_2-coated discs (1 coat, 250 mM; 2 coats, 480 mM) were placed in a corrosive environment with a pH of 12.4 (H_2O with NaOH). The Anodiscs[TM] coated with ZrO_2 were much more resistant to the corrosive nature of the solution and dissolved much more slowly than the uncoated Anodisc[TM] (24 h, 2 coats, 480 mM; 10 h, 1 coat, 250 mM; compared to 15 min for the uncoated).§

The uniform, conformal nature of the coatings is astonishing for a solution coating technique. The ability to coat porous materials without blocking the pores is believed to be a result of the binding of the metal precursor to the polymer. By binding the metal to the polymer in an aqueous solution, metal oxide formation becomes the last step in the film coating process, unlike the sol–gel technique, in which metal oxide polymer species begin to form, even in the bulk solution. In the PAD process, the pores of the

Fig. 3 MXRF 2D analysis of the membrane (480 mM; 1 coat). 10 μm spot size, 50 kV, 0.4 mA and integration time 100 s.
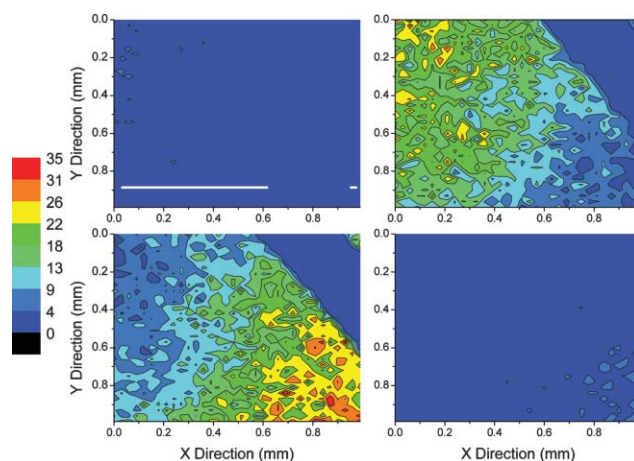
Fig. 4 Confocal MXRF depth profile of Zr in the membrane. 30 μm spot size, 50 kV, 0.5 mA and 50 μm step.

membrane are filled with the aqueous polymer solution, which is approximately 5 wt% metal content. During the initial thermal treatment water is removed, leaving behind metal-bound polymer. It appears that the removal of the water causes a contraction of the film that maintains the porosity of the disk, while the metal bound polymer remains as a thin film along the walls of the membrane. The polymer then decomposes at a temperature around 450 °C and leaves behind the metal that forms an oxide coating. The advantages of this technique include the ability to coat porous materials, the ease of scale-up (since it is a solution process) and the ease of processing (as no vacuum or volatile precursors are needed).

Fig. 2 MXRF of elemental Zr (250 mM; 1 coat) spectral image of the Anodisc[TM]. EDAX Eagle II, 20 kV, 100 μA, spot size 50 μm and integration time 100 s.

Notes and references

‡ Dipotassium ethylenediaminetetraacetic acid (1.00 g, 2.47 mmol) was dissolved in 30 mL of water. Zirconyl nitrate (2.00 g, 3.02 mmol) followed by polyethyleneimine (1 g) were added and the reaction mixture stirred. The resulting solution was clear and had a pH of 8.0. This solution was placed in an Amicon filtration unit containing a PM10 filter, designed to pass materials having a molecular weight < 10,000 g mol^{-1}, and washed twice with water. The final viscosity of the solution was measured and found to be 5.3 mm^2 s^{-1}. The final concentration was found to be 250 mM Zr. A second similar solution was prepared and concentrated further to give a 480 mM Zr solution. The preparation of the Ti solution has been described previously.[1]

The solution of metal bound polymer was placed as a drop on a glass slide. The Anodisc^{TM} (0.2 μm membrane discs; 14 mm diameter) was then placed on the drop, allowing the solution to wet the membrane completely. Excess solution was removed by pulling the membrane across the glass slide. This was repeated after inverting the membrane. The Anodiscs^{TM} were baked in a Thermolyne 48000 furnace by ramping to 120 °C at 1 °C min^{-1}, followed by a 30 min dwell, ramping to 350 °C at 2 °C min^{-1}, followed by a 30 min dwell, ramping to 450 °C at 2 °C min^{-1}, followed by a 360 min dwell, and finally stepping back to room temperature. All heating was done under an atmosphere of air.

§ A pH 12.4 solution was prepared using NaOH and H$_2$O. Three Anodiscs^{TM} : (i) an uncoated, (ii) a singly-coated (with the 250 mM zirconium solution), and (iii) a doubly-coated (with the 480 mM zirconium solution) were each placed in glass vials. Approximately 5 mL of the NaOH/H$_2$O solution was added to each vial. After 15 min the uncoated Anodisc^{TM} had completely dissolved, while the two coated Anodiscs^{TM} maintained their structure. The singly-coated Anodisc^{TM} was completely dissolved after 10 h, while the doubly-coated Anodisc^{TM} did not completely dissolve for 24 h.

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