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Polymers of intrinsic microporosity in electrocatalysis: Novel pore rigidity effects and lamella palladium growth

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ABSTRACT

Two polymers (i) the polymer of intrinsic microporosity (or PIM) ethanoanthracene TB-PIM (P1, PIM-EA-TB, MW 70 kDa, BET surface area 1027 $m^2 g^{-1}$) and (ii) the structurally less rigid polymer based on dimethyldiphenylmethane units (P2, BDMPM-TB, MW 100 kDa, BET surface area 47 $m^2 g^{-1}$) are compared to highlight the benefits of the newly emerging PIM membrane materials in electrocatalysis and nano-structure formation. Binding sites and binding ability/capacity in aqueous environments are compared in films deposited onto glassy carbon electrodes for (i) indigo carmine dianion immobilisation (weakly binding from water–ethanol) and (ii) $PdCl_4^{2-}$ immobilisation (strongly binding from acidic media). Nano-lamella growth for Pd metal during electro-reduction of $PdCl_4^{2-}$ is observed. Electrocatalytic oxidation of formic acid (at pH 6) is investigated for P1 and P2 as a function of film thickness. The more rigid high BET surface area PIM material P1 exhibits "open-pore" characteristics with much more promising electrocatalytic activity at Pd lamella within polymer pores.

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1. Introduction

Polymers of intrinsic microporosity (PIMs) have emerged over the past decade [1,2] with potential applications in gas storage [2,3], in membrane separations [4–6], in heterogeneous catalysis [7], and as the active component for optical sensors [8]. The rigid and contorted polymer backbone of PIMs precludes efficient packing to generate novel properties due to permanent microporosity. To date, applications are all reliant on rapid molecular permeability, however, here we report the significance of intrinsic microporosity to facilitate rapid ion transport within electrochemical membranes, which may find application in a variety of devices including fuel cells [9].

Recently, the novel preparation of amine-containing PIMs based on a polymerisation reaction involving the formation of Tröger's base (TB) was reported [10]. Thus, 2,6(7)-diamino-9,10-dimethyl-ethanoanthracene was polymerised with dimethoxymethane in TFA to give PIM-EA-TB (P1, see Fig. 1). Similarly, the commercially available monomer, bis(4-amino-3-methylphenyl)methane, reacts to give polymer BDMPM-TB (P2) with TB linking groups.

Both polymers have similar chemical functionality (see Fig. 1), are obtained with high molecular mass (M_W >70,000 $g\,mol^{-1}$), and are highly soluble in chloroform. However, only P1 demonstrates intrinsic microporosity with an apparent BET surface area of 1027 $m^2 g^{-1}$ due to its highly rigid structure, as determined by nitrogen adsorption of powdered samples at 77 K. In contrast, P2 is non-porous (BET surface area = 47 $m^2 g^{-1}$) due to greater chain flexibility.

In this report these two polymers are compared when deposited as thin film on glassy carbon electrode surfaces. It is demonstrated that the design of polymer membranes with intrinsic microporosity has a considerable effect on the uptake and retention of redox active anions. Indigo carmine and $PdCl_4^{2-}$ are investigated. Nano-lamella-like growth of palladium metal within PIM pores is observed. The electrocatalytic activity of palladium metal within pores is contrasted. The rigid backbone of the PIM P1 is shown to provide active pores and good catalytic performance.

2. Experimental

2.1. Chemical reagents

Polymers PIM-EA-TB (P1, M_W = 70 kDa, BET surface area = 1027 $m^2 g^{-1}$) and BDMPM-TB (P2, M_W = 100 kDa, BET

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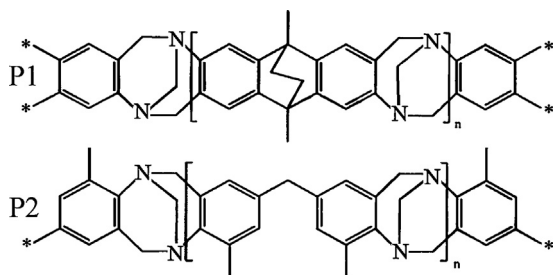*E-mail address:* F.Marken@bath.ac.uk (F. Marken).

Fig. 1. Scheme of molecular structures of P1 (PIM-EA-TB) and P2 (BDMPM-TB).

Fig. 2. (A) Photograph of a blue solution of indigo carmine and a yellow solution of $PdCl_4^{2-}$ as well as P1 membranes before and after immobilisation of the redox active colourants. (B) UV/vis spectra for (i) 100, (ii) 50, (iii) 10, (iv) 1, and (v) 0 μM indigo carmine in water–ethanol. (C) UV/vis spectra for P1 film (ca. 60 μm) after immersion in (i) 10 and (ii) 0 mM indigo carmine in pH 2 buffer. (D) UV/vis spectra for (i) 10, (ii) 5, (iii) 1, (iv) 0.5, and (v) 0 mM $PdCl_4^{2-}$ in 0.5 M HCl. (E) UV/vis spectra for a P1 film (ca. 60 μm) after immersion in (i) 10, (ii) 5, (iii) 1, and (iv) 0 mM $PdCl_4^{2-}$ solution.

surface area = 47 m^2 g^{-1}) were prepared from the trifluoroacetic acid (TFA) mediated reaction between dimethoxymethane and 2,6(7)-diamino-9,10-dimethyl-ethanoanthracene or bis(4-amino-3-methylphenyl)-methane, respectively, as reported previously [10]. Formic acid, palladium dichloride, perchloric acid (70%), hydrochloric acid (30%), chloroform, ethanol, sodium hydroxide, and phosphoric acid (85%) were obtained from Aldrich or Fisher Scientific and used without further purification. Solutions were prepared with filtered/deionised water of resistivity 18.2 MΩ cm from a Thermo Scientific water purification system (Barnstead Nanopure). Nitrogen was employed to de-aerate solutions prior to measurements.

2.2. Instrumentation

An Autolab potentiostat system (PGSTAT12, EcoChemie, The Netherlands) was employed with glassy carbon working electrode (3 mm diameter, BAS), a Pt wire counter electrode, and a KCl-saturated calomel reference (SCE, Radiometer, Copenhagen).

2.3. Procedures

The polymers P1 or P2 were completely dissolved into chloroform (1 mg in 1 mL solvent) by ultrasonication for 15 min. PIM films on glassy carbon electrodes were prepared by deposition of typically 5 μL solution and solvent evaporation. For indigo carmine experiments PIM or polymer coated electrodes were immersed into indigo carmine in phosphate buffer pH 2 (50 vol% ethanol) and then transferred to aqueous phosphate buffer for voltammetry. For $PdCl_4^{2-}$ experiments, PIM or polymer coated electrodes were immersed into 0.5 M HCl solution containing 0.05 M $PdCl_2$, rinsing with water, and transferring into a clean 0.1 M perchloric acid solution for Pd electro-deposition. The PIM containing Pd-coated glassy carbon electrode was then transferred into 0.1 M formic acid in 0.1 M phosphate buffer solution pH 6 for measurements.

3. Results and discussion

3.1. Effects of intrinsic microporosity I: indigo carmine uptake and reactivity

In order to investigate the electrochemical properties of PIM versus non-porous polymer films, solutions in chloroform (1 mg in 1 mL) were deposited onto 3 mm diameter glassy carbon electrodes and evaporated to dryness to give polymer film deposits. Comparison of voltammetric responses for films of P1 and P2 materials alone suggest no intrinsic electrochemical responses (vide infra). However, the microporous films are able to incorporate redox active anions (to complement the intrinsic ammonium
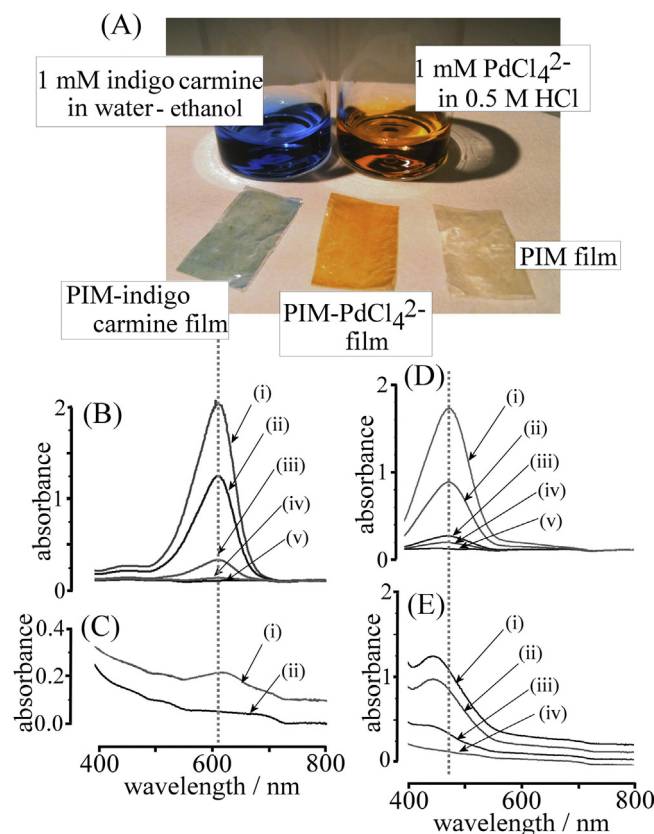
cation charge in the polymer backbone) such as indigo carmine. When PIM films are immersed into 1 mM indigo carmine in water, no significant uptake occurs (based on voltammetry). Similarly, a free-standing PIM film is not coloured under these conditions.

There are two methods of "opening pores" or "swelling" PIM materials for the more rapid exchange/uptake of anions such as indigo carmine: (i) addition of organic solvent such as ethanol or (ii) employing more acidic solution conditions. Both can be employed successfully for the immobilisation of indigo carmine. Fig. 2(A)–(C) show how indigo carmine at pH 2 (in the presence of 50 vol% ethanol) can be used to colour a free-standing (ca. 60 μm thickness) P1 membrane.

The extinction coefficient for indigo carmine monomer $\varepsilon_{IC} = 20,000$ M^{-1} cm^{-1} in solution [11] allows an estimate for the concentration of indigo carmine in the P1 membrane to be obtained (assuming a constant ε_{IC}). Based on data in Fig. 2(C) the apparent concentration of indigo carmine in the P1 film is ca. 0.8 mM. This compares to the apparent concentration of cationic binding sites estimated as 2.5 M (see structure in Fig. 1; assuming a density of about 1 g cm^{-3}). Binding of indigo carmine under these conditions appears to be dominated by factors other than electrostatic or only a fraction of the Tröger base sites are protonated/accessible (vide infra).