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Tuneable ion-selective inorganic membranes

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Abstract

A new type of ion-selective ceramic membrane with electrically tuneable selectivity is reported. The membrane consists of a conventional supported γ-alumina membrane with porous gold electrodes sputtered on both sides. An electrical potential difference can be applied over the electrodes. The transport of Cu^{2+} ions was investigated as a function of the applied field strength over the membrane and the copper concentration in the feed solution. It is shown that the transport rate can be tuned efficiently by the magnitude and direction of the field. This technology may find application in micro-fluidic devices such as micro total analysis systems.

Keywords: Inorganic membranes; Mesoporous; Transport; Electrical potential; Ion-selectivity

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1. Introduction

After synthesising and mounting the membrane in a separation module, it becomes a passive, unchanging semi-permeable barrier of which the separation properties can be varied only by variation of external process variables such as concentration difference, pressure difference, temperature, pH, etc.

New membrane concepts in which the intrinsic membrane properties are tuneable to some extent emerged only recently [1–3]. Farrusseng et al. [1] reported a vanadium oxide-based gas separation membrane with variable pore sizes, that can be set by variation of the oxygen partial pressure of the environment. Lee and Hong [2] and Kang and Martin [3] employed electrical potential differences to modify the membrane properties in order to selectively remove either negatively or positively charged components from a liquid mixture.

The aim of the present study is to use supported γ-alumina ceramic membranes and employ the same concepts of selective separation by electrical

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tuning. Ion-selective tuneable membranes are studied for small-scale applications in microfluidics, such as micro-total analysis systems (μTAS) and micro-chemical devices. Now, most μTAS approaches use miniaturised versions of conventional architecture and components to achieve system tasks. The ability to build materials with switcheable molecular functions could provide completely new approaches to valves, chemical separation and detection. Switcheable molecular membranes and the like could replace several mechanical components, leading to smaller devices, lower power consumption, and improved accuracy. Preliminary results from transport studies of copper ions through these membranes are presented here. A schematic drawing of the membrane used for these experiments can be seen in Fig. 1. It consists of two components: a macroporous support (pore size ~100 nm) and a thin mesoporous layer (pore size ~2 nm) with separation ability, with gold sputtered on opposite sides. In contrast to the pressure-driven nanofiltration process, the driving force for ion-selective permeation is the applied potential difference over the membrane, which promotes the transport of ions, but not the solvent. Overall charge neutrality is maintained by carrying out the process in a suitable electrolyte buffer solution. The primary aim is to arrive at highly selective, tuneable ion fluxes.

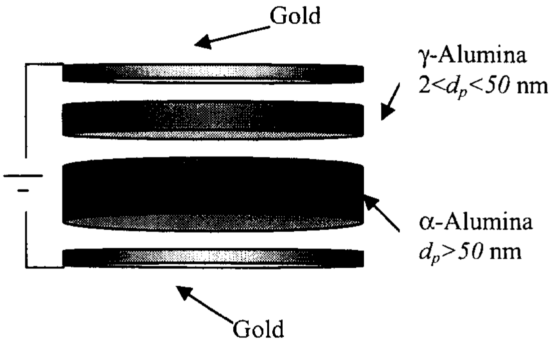

Fig. 1. Schematic diagram showing an electrically tuneable membrane.

2. Experimental

2.1. Membrane preparation

α-alumina was used as the macroporous support and dip coated with a mesoporous γ-alumina layer. The method of preparation of the α-alumina support and the method for coating the γ-alumina layers have been well documented in literature [4–7]. For a detailed description of supported γ-alumina membrane synthesis the reader is referred to [4]. Laterally conductive gold layers were sputtered on opposite sides of the α/γ-alumina composite membrane at room temperature. The membrane thickness is 0.22 cm.

2.2. Transport experiments

The experimental set-up for the transport experiments is shown in Fig. 2. The membrane was placed between the two halves of a U-shaped tube, with the separation layer at the feed side. A solution of 250 ml was added to the two cells on either side of the membrane. The solution at the permeate side contained 1.34 mmol/l KCl electrolyte, while the feed side solution consisted of the same electrolyte solution and a variable concentration of $CuCl_2$ in the range of 0.29–6.04 mmol/l. The pH was monitored throughout the experiments and was found to be between pH 5 and 6, for both the feed and the permeate side. Prior to the

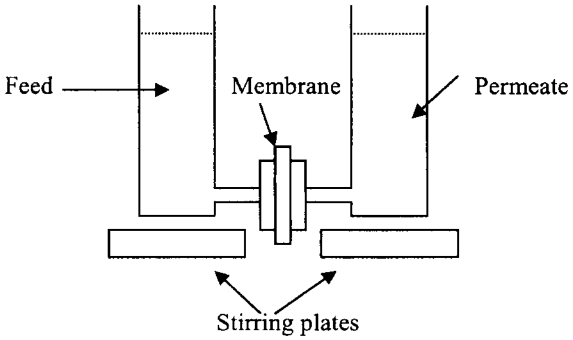

Fig. 2. Schematic drawing of the experimental set-up for the transport experiments.

experiments the membranes were left over night in water to ensure complete wetting of the membrane. An electrical potential difference was applied over the membrane using a potentiostat (MP 81 Bank Elektronik). All potentials reported here are given relative to the electrode potential at the feed side. The potential difference over the membrane can be defined as $\Delta V = V_f - V_p$, where ΔV is the potential difference over the membrane, V_f the potential at the feed side and V_p the potential at the permeate side. The absolute potential difference between the two membrane faces was kept sufficiently small to prevent electrolysis of water. From here on the potential difference will be expressed in terms of field strength.

The transport of Cu^{2+} through the membrane was analysed by extracting 1 ml from the permeate solution at fixed intervals and determining the copper concentration by atomic absorption spectrometry (AAS).

3. Results and discussion

Fig. 3 shows the effect of the field strength on the transport properties of the membrane over a period of time. Here the field strength over the membrane was changed from +4.55 to 0, and then to –4.55 V/cm (ΔV = +1, 0 and –1 V, respectively). As can be seen in Fig. 3a this has a profound effect on the transport rate of copper ions. When the

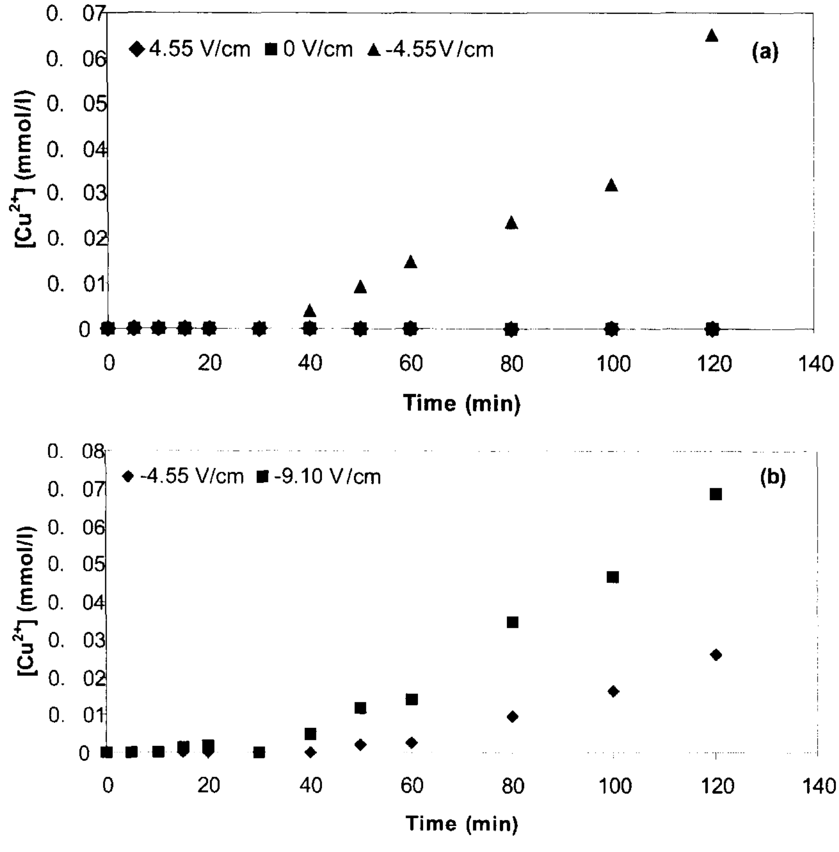

Fig. 3. Transport of copper ions through the membrane vs.time (a) for initial copper concentration of 6.04 mmol/l and (b) of 3.04 mmol/l.

field strength is +4.55 or 0 V/cm, no net transport of copper ions through the membrane can be observed. But this changes when the field strength over the membrane is –4.55 V/cm. This effect is also illustrated in Fig. 3b where the field strength was increased from –4.55 to –9.10 V/cm. As can be seen in Figs. 3a and 3b there is an induction period of which the cause is not yet fully understood. The transport of copper ions increases with increasing field strength. For the positively charged copper ions the direction of the electrical field is such that it enhances transport of the copper ions. This means that if a positive field is generated over the membrane, the diffusion of copper ions will be blocked, even if there is a concentration gradient over the membrane.

The flux of Cu^{2+} ions can be described using Onsager's equation

$$J_{Cu^{2+}} = -L_{Cu^{2+}} \frac{d\eta_{Cu^{2+}}}{dx} = -K_1 \frac{dc}{dx} - K_2 \frac{d\psi}{dx} \quad (1)$$

where J_{Cu2+} is the flux of copper ions, L_{Cu2+} is the Onsager coefficient, K_1 and K_2 are proportionality factors, $\frac{d\eta_{Cu^{2+}}}{dx}$ is the electrochemical potential gradient, $\frac{dc_{Cu^{2+}}}{dx}$ is the concentration gradient and $\frac{d\psi}{dx}$ is the electrical potential gradient. This implies that applied field strength as well as concentration difference act as driving forces. If the electrical field over the membrane is set to 0 V/cm no transport of ions is observed. That suggests the term $-K_1 \frac{dc}{dx}$ is negligible. But when the experiments were repeated with membranes consisting only of the gold-sputtered α-alumina support, net transport of copper ions at 0 and +4.55 V/cm was observed, in contrast to the observations made in Fig. 3a. This implies that the γ-alumina mesoporous layer is necessary to achieve good tuneability by eliminating the diffusional component of the flux. However, the transport rate of copper ions is promoted by the concentration of copper ions in the feed. This is evident in Fig. 4. Here the concentration of ions in the feed was increased while the field strength was kept constant at –4.55 V/cm. This suggests that proportionality factor K_2 is a function of the concentration of copper ions.

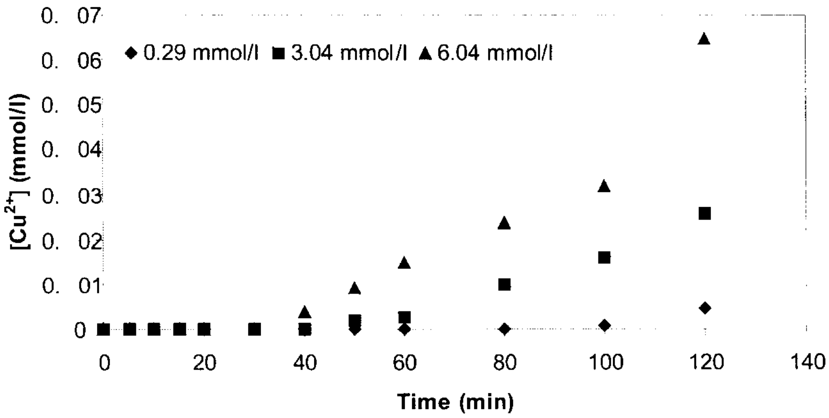

Fig. 4. Effect of the variation of Cu^{2+} concentration in the feed on the transport rate. Field strength applied over the membrane is –4.55 V.cm^{-1}.

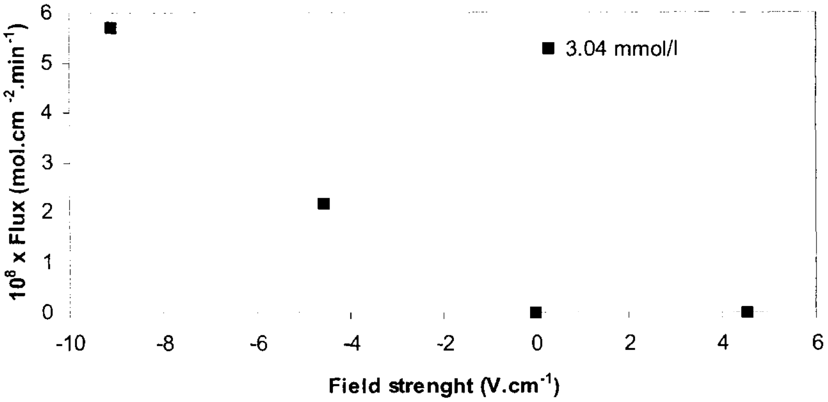

Fig. 5. Flux vs. applied field strength for the copper transported through the membrane.

From the slope of the graphs in Figs. 3 and 4 the Cu^{2+} flux was calculated. The calculated flux shown in Fig. 5 falls in the range of 0–10^{-8} mol. cm^{-2}.min^{-1}. Within this range they can be set to any arbitrary value by manipulation of the potential difference. Lee and Hong [2] and Kang and Martin [3] employed slightly different approaches to achieve tuneable separation. Lee and Hong [2] used a stacked membrane consisting of two polypyrrole-coated porous layers and a microporous polycarbonate filter sandwiched between them. By applying a potential difference between the outer layers, migration of ions through the pores was observed. On the other hand, the approach employed by Kang and Martin [3] was to take a ceramic membrane with straight mesopores and coat the surface and the inside of the pores with gold. The membrane surface was then charged relative to the potential of the feed solution. As the pores were sufficiently small for the double layer to penetrate the entire pore diameter, an ion-selective membrane was obtained. When the membrane surface was negatively charged, predominantly cationic fluxes were observed, and vice versa.

4. Conclusions

It was shown that electrically tuneable ion-selective inorganic membranes can be made. These membranes show reasonable Cu^{2+} fluxes with a very good tuneability. Future research will focus on the investigation of other cations, anions, mixtures thereof and amino acids.

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