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## Journal of Membrane Science

journal homepage: [www.elsevier.com/locate/memsci](http://www.elsevier.com/locate/memsci)

# Study of ionic transport through metalized nanoporous membranes functionalized with self-assembled monolayers

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## ARTICLE INFO

## Article history:

Received 22 January 2014

Received in revised form

27 February 2014

Accepted 5 March 2014

Available online 15 March 2014

## Keywords:

Permselectivity

Interfacial transport

Self-assembled-monolayers

Ionic transport

Metalized nanoporous membranes

## ABSTRACT

Ionic transport through synthetic nanoporous membranes has received great attention in applications related to biosensing, fuel cell, and desalination. Past work has demonstrated that charge selectivity can be achieved by applying a potential across a metallized conductive membrane. However, challenges arise for improving charge selectivity as a result of irreversibility of the system from the anion adsorption at the membrane surface. This study demonstrates how charge selectivity can be improved with the presence of a well grown self-assembled monolayer (SAM), which can aid in applications that use chemical separation processes based on the surface charge of the nanopore.

In this work, the transport and selectivity properties of gold-coated conductive nano-capillary-array-membranes (NCAMs) are studied using charged species methyl viologen paraquat, ( $MV^{2+}$ ) and naphthalenedisulfonate disodium salt ( $NDS^{2-}$ ). The selectivity coefficients for  $MV^{2+}$  and  $NDS^{2-}$  increased with the functionalization of undecanethiol on the gold-coated NCAM surface. With the presence of a SAM, the selectivity coefficients increased by 44% for  $MV^{2+}$  and 200% for  $NDS^{2-}$ . The influence of ionic transport from the diffuse layer potential at the walls and surface of the nanopore is also discussed.

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## 1. Introduction

Nanoporous membranes have received great attention in the fields of water desalination, biosensing, and chemical separations [1–17]. There have been numerous studies for the separation of biomolecules and analytes based on charge selectivity [18–23]. It has been demonstrated that proteins can be separated by applying potentials across conductive alumina membranes [24]. Cheow et al. developed a platinum coated nanoporous alumina membrane to demonstrate the permselectivity of proteins by applying different potentials across the membrane [25]. Several studies have also been done demonstrating charge selectivity through nanoporous membranes [26–31]. Studies have included fabrication of ion-tracked polyethylene terephthalate membranes, with the membrane surface terminated with carboxylate terminal groups [3]. The membrane's selectively transported cations and

prevented migration of anions. Attaching amino moieties on the membranes surface and pore wall proved to reverse the selective properties of the membrane. It has also been demonstrated that functionalizing gold nanotubule membranes with self-assembled monolayers (SAMs) could alter the pH responsiveness of the membrane [32]. Selective transport through nanopores has also been found to be dependent on the hydrophobic interaction between the analyte and membrane surface. Zenglian et al. used an electroless gold-deposited PCTE membrane modified with a hydrophobic terminated thiol surface. The competing effects between the interactions of the entrance and surface of the nanopore were compared. It was concluded that the entrance effect had the most influence on the transport of analyte across the nanopores [33].

Several studies have shown that anion adsorption on a conductive NCAM surface can affect the exclusion enrichment effect of coions and counterions. Mun et al. demonstrated charge selectivity using electroless gold coated polycarbonate track etched membranes (PCTE) [34]. The PCTE membranes are fabricated by bombarding a polycarbonate film with a collimation of high-energy nuclear fission fragments, which results in damaged

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<sup>1</sup> This paper is dedicated to the memory of Professor Mark A. Shannon, the authors' advisor and mentor, who recently passed away.

tracks through the film. The damaged tracks are then etched by an aqueous base solution to create cylindrical pores within the polycarbonate film [35]. The PCTE gold-coated surface was functionalized with propanethiol for the prevention of anion adsorption (e.g. chloride ions) on the surface of the membrane. However, it was observed that the permselectivity of the membrane was inhibited when positive potentials (anodic) were applied at the membrane surface. It was concluded that the poor quality of SAM layer led to irreversibilities on the charge selective system as a result of adsorption of anions. Although the membrane was immersed in thiol solution for 24 h, studies have shown that more allocated time is necessary to grow a well ordered (SAM) [36–38]. The authors have shown that detection of analytes can be achieved by interactions with the membrane surface/pore wall [39–41]. Schmuhl et al. investigated electric field-driven transport of ions through supported mesoporous  $\gamma$ -alumina membranes, with surfaces metalized with gold [42]. The studies showed that the electrolyte composition could affect the flux of copper ions through a permselective membrane. It was demonstrated that the flux of copper ions ( $\text{Cu}^{2+}$ ) was enhanced by the presence of adsorbed chloride ions on the gold-coated alumina surface. The same experiments were done with solutions containing fluoride ( $\text{F}^-$ ) and nitrate ( $\text{NO}_3^-$ ) ions. Flux enhancement of  $\text{Cu}^{2+}$  was not present when electrolyte solutions containing  $\text{F}^-$  and  $\text{NO}_3^-$  were used. As a result from XPS analysis, it was found that chemisorption of chloride on to the gold-coated membrane surface occurred, resulting in a negatively charged surface. It was concluded that the negatively charged membrane surface led to a local accumulation of counter ions, which enhanced the flux of  $\text{Cu}^{2+}$  ions.

If specific adsorption of a molecule occurs on the surface of a membrane, ion selectivity for separation will be inhibited by the loss of interaction between the membrane surface and analyte as shown in Fig. 1a. If the membrane surface is well covered by the SAM in order to minimize ion adsorption, ion selectivity can be enhanced for a specific molecule of interest (Fig. 1b).

The applications of SAMs are often limited by the immersion time allocated for the growth of the SAM. Past work has focused on studying the properties of a well-ordered SAM by electrochemical impedance spectroscopy (EIS) [37,43]. It was found that a minimum of 48 h is needed to grow a well-ordered SAM [37,38].

Surface functionalization is crucial for bioseparation and biosensing applications. Savariar et al. functionalized the surface of a polymeric membrane with  $\text{SnCl}_2$ , which led to the separation of analytes by electrostatic and hydrophobic interactions [44]. Additional work has focused on studying the transient current response based on the interaction between proteins and walls of single nanopores [41,45]. Wei et al. were able to immobilize proteins by using an  $\text{OH}^-$  terminated thiolated SAM to act as a protein receptor. The interaction between the protein and nanopore wall can be quantified by the time constant associated with adsorption and desorption events. Without the presence of a SAM on the surface, non-specific protein adsorption can occur on the walls of the nanopore. This can lead to effective blockage within the nanopore with non-targeted proteins, leading to a smaller measurable current (lower  $S/N$  ratio) across the nanopore [41]. Moreover, redox currents typically increase the background noise for electrochemical sensors. If detection can be accomplished with lower applied potentials,  $S/N$  ratios can be improved for electrochemical sensing of specific analytes [46].

In this work, we study the transport of methyl viologen (paraquat,  $\text{MV}^{2+}$ ) and naphthalenedisulfonate disodium salt ( $\text{NDS}^{2-}$ ) across a conductive NCAM while applying a range of potentials with respect to the membrane surface at the entrance side. A polycarbonate track etched (PCTE) membrane was made conductive by sputter coating gold on the membrane surface. Transport studies were done in a voltage range in which faradaic current was minimized at the surface of the gold-coated nanopore. The goal of the transport studies is to demonstrate improved charge selectivity when a well-grown 1-undecanethiol monolayer is assembled at the

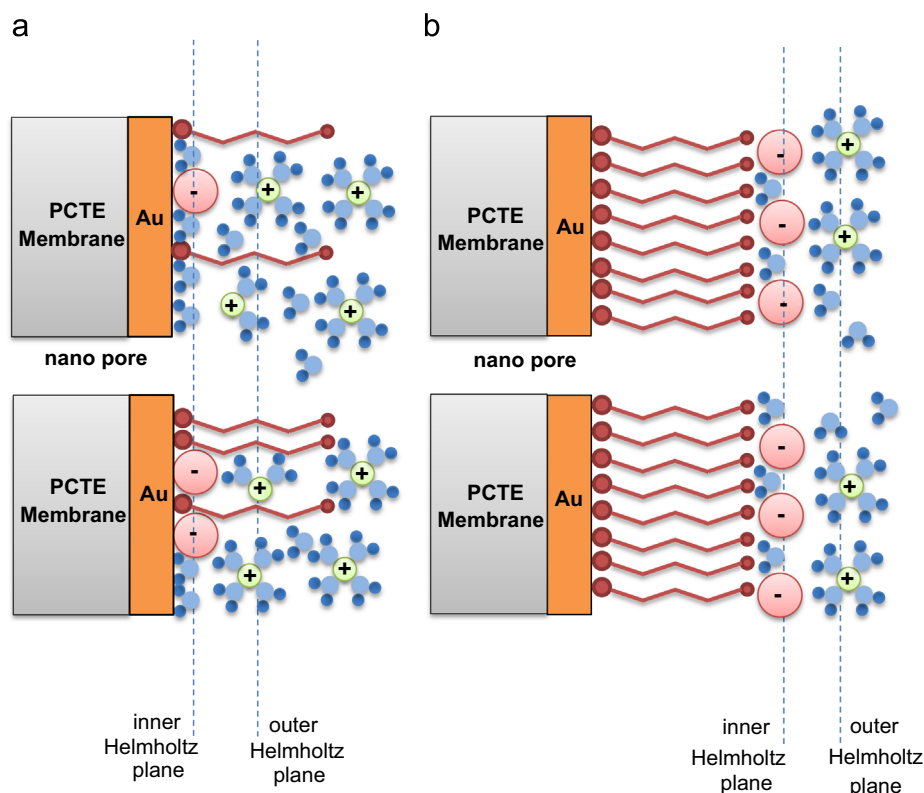


Fig. 1. Schematics (a) and (b) of a gold coated NCAM, which illustrates the improvement when a well-grown SAM is attached to the monolayer.

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