



Nanoscopic liquid/liquid interface arrays supported by silica isoporous membranes: Trans-membrane resistance and ion transfer reactions



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ABSTRACT

Miniaturization of the interface between two immiscible electrolyte solutions (ITIES) brings the benefits of enhanced mass transport in comparison with the macroscopic ITIES, similar to those observed with an ultramicroelectrode. In this work, ultrathin free-standing silica isoporous membrane (SIM, 80 nm in thickness) consisting of a high density of perforative channels with a uniform size (2–3 nm in diameter) was used to construct nanoscopic ITIES (nano-ITIES) arrays. Electrochemical characterization of the nano-ITIES array by studying the ion-transfer voltammetric behavior of tetra-*n*-propylammonium (TPRA⁺) suggested the domination of hemispherical molecular diffusion. The effect of trans-membrane resistance on the heterogeneous ion transfer was investigated by varying the supporting electrolyte concentration in both phases, which was found to be negligible due to the ultrathin thickness and high channel density of SIM. In addition, the nano-ITIES array exhibited excellent charge selectivity towards ionizable species due to the overlap of electrical double layer in the ultrasmall silica channels, which could be modulated by the supporting electrolyte concentration, aqueous solution pH and channel surface modification. These findings provide the basis for the nano-ITIES array to be used in ion detection and separation.

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1. Introduction

Electrochemistry at the liquid/liquid interface, or so-called the interface between two immiscible electrolyte solutions (ITIES), with capability of detecting molecules that are ionizable but redox inactive, enables the label-free molecular detection based on the current signal caused by the ion transfer across the interface [1,2]. For example, it allows the detection of various metal ions [3,4], drugs [5,6], dendrimers [7] and biomolecules, such as neurotransmitters [8,9], peptides [10,11], proteins [12,13] and DNA [14]. Furthermore, similar to ultramicroelectrodes, a miniaturized ITIES has advantages of enhanced mass transport and suppressed ohmic drop. Thus, at the miniaturized ITIES the analytical performance can be remarkably improved with an enhanced analytical sensitivity and decreased limit of detection (LOD) [15,16]. If the size of ITIES is reduced to the nanoscale, the sensing capacity can be further improved [2]. Moreover, at a sufficiently small nanoscopic ITIES (nano-ITIES), ion transfer will be dominated by the molecular properties, such as size and charge. In addition, new physical phenomena will also come to play an important role in ion transfer processes, e.g. the permselective ion transport across the ITIES arising from the strong overlap of electrical double layer (EDL).

Two main approaches have been reported so far to build nano-ITIES, either by establishing it at the orifice of a nanopipette [17,18,19] or by

supporting it with nanoporous materials [20,21]. The latter one has benefits of increased magnitude of current and constraint of numerous nanointerfaces to a defined geometry [22]. Dryfe and Kralj have primarily utilized nanopores/nanochannels on track-etched polymers [20], anodic aluminum oxide [23] and silicate zeolite membranes [24,25] to support nano-ITIES arrays. The nano-ITIES arrays templated by silicate zeolites with pore size below 1 nm allows of attaining size and charge selective transfer of ionic species across the ITIES. Recently, Arrigan and coworkers have performed a series of studies by supporting ITIES with nanopore arrays drilled on silicon nitride membranes by electron-beam lithography [26] or focused ion-beam milling [27]. The size of individual ITIES can be as small as 17 nm. Chen et al. have presented an approach for building nano-ITIES arrays using the hybrid mesoporous silica confined in channels of porous polymer membranes, where the individual interface size can approach the molecular scale [28]. Other than aforementioned ex-situ preparation strategies, mesoporous silica films in-situ deposited at the macroscopic or microscopic ITIES, as reported by Walcarius et al. [29,30,31], have also been utilized to support nano-ITIES arrays with obvious molecular selectivity in terms of size and charge. More recently, we have demonstrated the use of ultrathin free-standing silica isoporous membrane (SIM) consisting of straight and perforated channels for supporting the nano-ITIES arrays [32]. The created arrays process a well-controlled and reproducible interface structure. Moreover, due to the uniform channel size, the arrays displayed a precise selectivity according to molecular size and charge.

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Herein we report a detailed electrochemical study on the SIM-supported nano-ITIES array by ion transfer voltammetry. The previous work reported by our group has verified the formation of nano-ITIES array under the support of SIM, which displayed the size-selectivity towards the heterogeneous ion transport [32]. In this work, we first measured the ion-transfer voltammetric response of tetra-*n*-propylammonium (TPrA⁺), which displayed a steady-state sigmoidal current curve and verified the domination of hemispherical molecular diffusion. Then, the effect of trans-membrane resistance on the ion transfer behavior of TPrA⁺ and tetrabutylammonium (TBA⁺) was investigated by varying the concentration of electrolytes in both phases. Finally, the charge-selectivity of nano-ITIES array arising from the overlap of electrical double layer in ultrasmall silica channels was investigated. Using tris(2,2'-bipyridine)ruthenium(III) as the model ion, we found that its transfer across the nano-ITIES could be modulated by the supporting electrolyte concentration, aqueous solution pH and channel surface modification.

2. Experimental section

2.1. Chemicals and materials

All chemicals were used as received without further purification. 1,2-Dichloroethane (DCE, HPLC grade), lithium sulfate (Li₂SO₄, 99.9%) and sodium *p*-toluenesulfonate (TsO⁻Na⁺, 96%) were ordered from Aladdin. Lithium chloride anhydrous (LiCl, ≥97%) was obtained from Hengxin Chemicals. Hydrochloric acid (HCl, 37%) and sulfuric acid (H₂SO₄, GR) were ordered from Sinopharm. Tris(2,2'-bipyridine)ruthenium(III) dichloride (Ru(bpy)₃Cl₂, 98%) was provided by Acros. *N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium chloride (TMAC, 50% in methanol) and potassium tetrakis(4-chlorophenyl)borate (KTPBCl, 98%) were provided by TCI. Bis(triphenylphosphoranylidene)ammonium chloride (BACl, 97%) and tetra-*n*-propylammonium chloride (TPrACl, >99%) were received from Alfa Aesar. BATPBCl was prepared by metathesis of 1:1 mixture of BACl and KTPBCl in methanol/water mixture (V:V = 2:1). Indium tin oxide (ITO) coated glass (<15 Ω/sq, 100 ± 20 nm) was purchased from Zhuhai Kaivo. Silicon nitride (SiN, 150 nm in thickness) coated silicon wafer (10 mm × 10 mm frame dimension) with a 1 mm × 1 mm window consisting of a single 18-μm-diameter micropore in the window center, designated as the SiN window, was ordered from Risun Instrument.

2.2. Preparation and modification of free-standing SIM

The Stöber-solution growth approach was utilized for the synthesis of SIM on the ITO coated glass (see details in Section S1 of the Supporting information) [33]. The integrity and permeability of SIM was characterized by electrochemistry and electron microscope

measurements (see results in Figs. S1 and S2). The thickness of SIM is ca. 80 nm (see Fig. S2). The free-standing SIM with perforated channels was prepared by exfoliating SIM from the ITO surface and transferred to the SiN window (see details in Section S2 and Fig. S3 in the Supporting information) [34]. Modification of SIM surface was performed as reported previously [35]. Typically, the SIM/SiN chip was firstly dried at 100 °C for 2 h and subsequently immersed in 1% TMAC/dichloromethane (V/V) for 4 h at room temperature. The chip was then washed by dichloromethane and ethanol, and finally heated at 80 °C for 2 h. The surface modification by TMAC was verified by the voltammetric behavior of modified SIM that was opposite to the unmodified SIM (see details in Section S3 and Fig. S4 in the Supporting information). The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements were performed on a SU8010 field-emission scanning electron microscope (Hitachi, Japan) and a HT7700 transmission electron microscope (TEM) (Hitachi, Japan), respectively.

2.3. Electrochemical measurements

All liquid/liquid electrochemistry measurements were performed on a CHI 920 electrochemical workstation (CH Instrument, Shanghai) at ambient temperature (20 ± 2 °C) using a two-electrode configuration. A homemade U-tube cell with the SiN or SIM/SiN chip fixed in the middle was used, as shown in Fig. 1a. Silver/silver chloride (Ag/AgCl) and silver/silver sulfate (Ag/Ag₂SO₄) wires, serving as the reference electrodes, were placed in the aqueous solution and DCE reference solution, respectively. The electrochemical cells with electrolyte compositions used in this work are shown in Fig. 1b. LiCl and Li₂SO₄ were utilized as electrolytes in the aqueous phase, and BATPBCl as the electrolyte in the DCE phase. The DCE reference solution contained BACl (for study of electrolyte concentration effect as reported previously [36]) or BACl and LiCl. The background-subtracted voltammograms obtained in the forward potential scan were present unless otherwise specified.

3. Results and discussion

3.1. Characterization of SIM/SiN and nano-ITIES array

Fig. 2a and b display the top-view SEM images of the SiN chip before and after supporting a piece of SIM. An 18-μm-diameter micropore can be found on the SiN window even in the latter case, because the SIM is ultrathin. From the TEM image (see Fig. 2c), a large number of nanopores (appeared as bright spots) with a uniform size of 2–3 nm in diameter and a high pore density of 4.0 × 10¹² cm⁻² can be clearly identified [34]. Moreover, no any cracks were found on the SIM, even after being used for several times (see Fig. S5), suggesting the SIM has excellent mechanical and chemical stability.

The SIM/SiN-supported nano-ITIES array was characterized by ion transfer voltammetry of TPrA⁺ using the two-electrode system

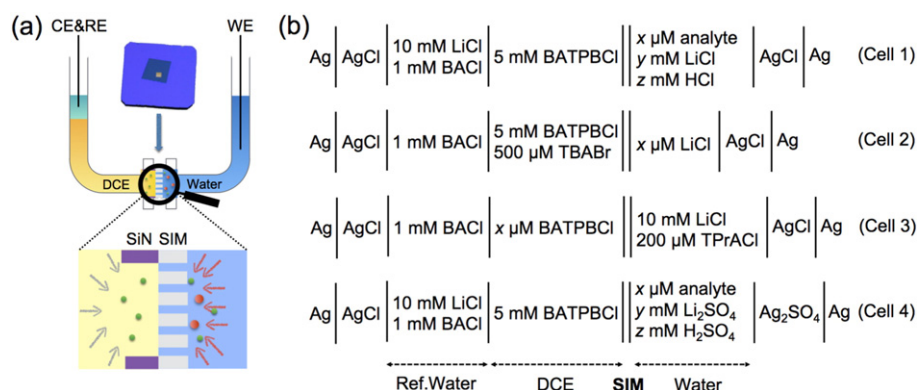


Fig. 1. (a) A home-made U-shaped glass cell. (b) Illustration of the electrolyte composition of electrochemical cells.

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