

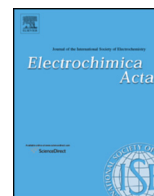


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Electrochemical characterization of liquid-liquid micro-interfaces modified with mesoporous silica

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ABSTRACT

In this work, the array of miniaturized interfaces between two immiscible electrolyte solutions was modified with a mesoporous silica material. The electrochemical behavior of such silica deposits was evaluated with six analytes: 3 tetraalkylammonium cations of different sizes, the anionic 4-octylbenzenesulfonate and two poly(aminoamide) dendrimers (generation 0 and 1). Presence of silica deposits affects the ion transfer across the liquid/liquid interface for all six probes with the effect greater for species possessing higher hydrodynamic radius. Analytical parameters (sensitivity and detection limit) were extracted from the calibration curves plotted in the presence and in the absence of silica deposits. Results indicate that silica constitutes an obstacle for interfacial transfer reaction and becomes limiting factor for interfacial mass transfer. Three main conclusions can be drawn from the experimental observations: (i) for tetraalkylammonium species, the larger species (tetrabutylammonium) is more affected by the presence of silica deposits than the smaller species (tetramethylammonium); (ii) due to the negative charge of silica walls, anions are more affected than cations of the same size; (iii) multiply charged cationic dendrimers are less affected by the presence of silica deposits than smaller single charge cations. Apparent diffusion coefficients for all species were also extracted from calibration curves plotted after modification.

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1. Introduction

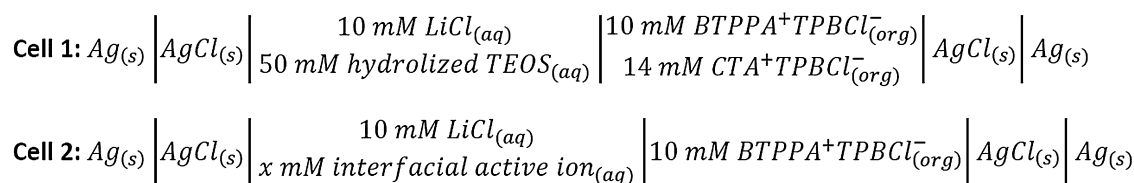
The interface between two immiscible electrolyte solutions (ITIES) as an electrochemical sensor is basically deprived of mechanical defects, it can be self-healing and it enables the detection of hydrophobic and hydrophilic species. Furthermore, the liquid/liquid interface can be miniaturized down to the micro- and nanoscale level [1–3], which improves the sensitivity (due to enhanced mass transport) and lowers the limit of detection (due to smaller capacitive currents). Both sensitivity and limit of detection are qualitative parameters indicative of a good analytical detection method. The range of ionic analytes detectable at the ITIES is broad, examples include: inorganic molecules – alkali metals [4]; small organic molecules – drugs [5], food additives [6]; synthetic and natural macromolecules – dendrimers [7–9], polyelectrolytes [10,11] and proteins [12–14], or species of biological importance [15,16]. Despite this broad range of targets, selectivity of the ITIES remains to be improved. Two approaches are taken to improve the

selectivity of the ITIES. The first one concerns the use of selective ionophores to favor the assisted transfer of ions [17], whereas the second approach deals with the *ex-situ* ITIES modification (with zeolite molecular sieve [18]).

In conventional electrochemical techniques – with working electrode being the solid conductor – weak selectivity is frequently solved *via* surface modification [19]. In this context, great attention was paid to mesoporous silica modifiers as they can be easily deposited onto solid substrate [20], they exhibit a high specific surface area and ordered three-dimensional structures [21] with chemical functionalities [22] can be formed. Under the suitable conditions, the formation of ordered and oriented mesoporous silica materials can be controlled. A method called ‘electro-assisted self-assembly’ employing a sol-gel process based on a surfactant template allows the formation of mesoporous silica with highly ordered symmetry of pores oriented perpendicular to the electrode surface [23,24]. In addition, choosing the suitable template allows the tuning of the pore sizes among the silica framework [25], which is of greatest interest for sensing devices. Template-based mesoporous silica found numerous applications: as immobilization host for biologically active molecules [26], in membrane separation processes [27], as templates in nanocasting formation

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Scheme 1. Electrochemical cells for silica electrodeposition (cell 1) and interfacial ions transfer study (cell 2).

of array of nanowires [28], in drug delivery [29] and finally in electroanalytical chemistry [30,31] and sensing [32]. In our previous works, we have shown that a sol-gel process based on a surfactant template can be easily performed at the macroscopic ITIES with the help of ion transfer voltammetry [33]. This requires the presence of hydrolyzed silica present in the aqueous phase and cationic surfactant – cetyltrimethylammonium cations (CTA^+) – in the organic phase. The interfacial polarization leads to the transfer of CTA^+_{org} to the aqueous phase and an interfacial silica deposit is formed upon self-assembly condensation. Subsequently, the protocol developed at macroITIES was adapted to the array of microITIES supported by silicon wafer [33]. Miniaturization provides good mechanical stability of electrogenerated free standing silica deposits and gives better electro-analytical response [34]. The mechanism for the formation of silica deposits was proposed based on electrochemical, Raman spectroscopy and electron microscopy studies [33–35].

Here, to go one step further, an array of liquid-liquid micro-interfaces was modified with silica deposits formed around a CTA^+ template and then characterized by ion transfer voltammetry of six different model ions: three cations from the tetralkylammonium family (tetramethylammonium TMA^+ , tetraethylammonium TEA^+ and tetrabutylammonium TBA^+), one anion (4-octylbenzenesulfonate, $4OBSA^-$), and two dendritic cations from the poly(aminoamide) dendrimer family (PAMAM generation G0 and G1). These ions differ in size, charge and chemical nature. The ion transfer potential and currents of these six ions before and after modification of the ITIES with mesoporous silica were compared. We investigate the influence of the ions characteristics (charge, z_i , diffusion coefficient, D and molecular hydrodynamic radius r_h) on analytical parameters such as sensitivity, limit of detection and apparent diffusion coefficient, and how the interface modification affected those characteristics.

2. Experimental

2.1. Chemicals

Bis(triphenylphosphoranyldiene) ammonium chloride, ($BTPPA^+Cl^-$, 97%, Aldrich) and potassium tetrakis(4-chlorophenylborate), (K^+TPBCl^- , $\geq 98\%$, Fluka), were used to prepare the organic electrolyte by metathesis reaction. Sodium chloride, ($NaCl$, $\geq 98\%$, Prolabo) and lithium chloride ($LiCl$, $\geq 99\%$, Aldrich) were used as the aqueous phase electrolytes. Cetyltrimethylammonium bromide ($CTAB$, $\geq 99\%$, Acros Organics) and K^+TPBCl^- were used for the preparation of template salt by metathesis reaction [33]. Silica precursor used in this study was tetraethoxysilane ($TEOS$, 98%, Alfa Aesar). The pH of the aqueous phase during hydrolysis ($pH = 3$) and condensation ($pH = 9.5$) of $TEOS$ was adjusted with solutions of 1 M HCl (1 M, volumetric solution, Riedel-de Haen) and 1 M $NaOH$ (from pellets, pure, Riedel-de Haen). Tetramethylammonium chloride (TMA^+Cl^- , $\geq 99\%$, Fluka), tetraethylammonium chloride (TEA^+Cl^- , $\geq 99\%$, Fluka), tetrabutylammonium chloride (TBA^+Cl^- , $\geq 99\%$, Fluka), 4-octylbenzenesulfonic acid sodium salt ($4OBSA^-$, 97%, Fluka), poly(aminoamide) generation 0 (PAMAM G0, 20% solution in methanol, Aldrich) and poly(aminoamide)

generation 1 (PAMAM G1, 20% solution in methanol, Aldrich) were employed for electrochemical characterization of silica material-modified liquid/liquid interface. The high density organic phase was a 1,2-dichloroethane (DCE , $\geq 99\%$, Sigma-Aldrich) whereas the low density phase was high purity H_2O obtained from a Millipore milli-Q water purification system. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99–102%, Fluka) was used to prepare silver/silver chloride reference electrodes.

2.2. Electrochemical cell

The electrochemical cell used in this work is the same as used previously [34]. The platinum mesh and a silver/silver chloride wire were used as aqueous counter and reference electrodes respectively. Organic phase was placed into the capillary to the end of which silicon wafer supporting the array of ITIES was attached. Wafer was fixed with Rubson® silicone acetate sealant. A silver/silver chloride wire spiral acted as both reference and counter electrodes for the organic phase. The μ ITIES array were patterned by photolithography and pierced by a combination of deep ion reactive and wet etches as described elsewhere [36]. A μ ITIES array was made of 30 pores of 5 μm radius separated by 200 μm . All electrochemical experiments were run with a PGSTAT 302 N from Autolab (Metrohm, Switzerland), with a four electrode set-up.

2.3. Interfacial silica electrodeposition and ion-transfer study

Two electrochemical cell configurations were used (Scheme 1), one for the silica deposition (cell 1) and the other one for electrochemical characterization of the modified μ ITIES by ion transfer voltammetry (cell 2).

Silica material at liquid/liquid interface was electrodeposited by cyclic voltammetry (Fig. 1) at 5 $mV s^{-1}$ using electrochemical cell 1. On the forward scan, CTA^+ ions are transferred from the organic to the aqueous phase, which triggered the condensation of silica. On the reverse scan, CTA^+ adsorbed on the silica deposited are

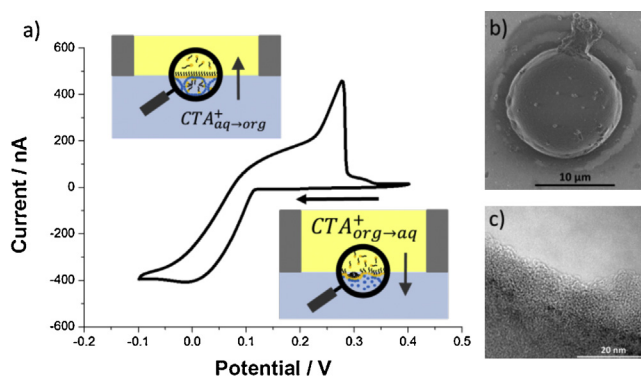


Fig. 1. a) Typical cyclic voltammogram recorded during silica electrodeposition at an array of miniaturized ITIES. The arrow indicates the scan direction. Concentration of $CTA^+ = 14 \text{ mM}$ and $TEOS = 50 \text{ mM}$, scan rate = 5 $mV s^{-1}$ b) Top-view scanning electron micrograph of a single modified pore and c) Transmission electron micrograph of mesoporous silica.

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