Optical Response of Porous Titania-Silica Waveguides to Surface Charging in Electrolyte Filled Pores

by **Jan Sefcik**, **Marek Kroslak**, and **Massimo Morbidelli***

Laboratorium für Technische Chemie, ETH-Hönggerberg/HCI, CH-8093 Zürich
(tel.: +41-1-6323034; fax.: +41-1-6321082; e-mail: morbidelli@tech.chem.ethz.ch)

Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

In this work, we present a novel method for *in situ* investigation of surface charging and ion transport inside nanopores of titania-silica waveguide by means of the optical-waveguide-lightmode spectroscopy. Porous oxide waveguides show a strong optical response when exposed to electrolyte solutions, and this response is consistent with oxide surface charging due to changes in ionic strength and pH of the solution in contact with the waveguide. The optical response to pH or electrolyte concentration change is stabilized within several minutes when the solution ionic strength is sufficiently high (0.1M), while it takes two orders of magnitude longer to reach stable optical response at very low ionic strengths (< 0.1mM). The relaxation times at the high ionic strength are still by several orders of magnitude slower than expected from bulk diffusion coefficients of electrolytes in water. Our results indicate that diffusion of electrolytes is severely hindered (and more so with decreasing ionic strength) in charged pores inside waveguides.

1. Introduction. – Sol-gel-based silica-titania mixed oxides are important materials in catalysis [1][2] and optical applications [3–5]. Sol-gel synthesis typically involves one or more metal alkoxides undergoing hydrolysis in aqueous solutions and subsequent condensation eventually forming particles or gels [6]. Resulting materials are usually nanoporous with substantial internal surface areas on the order of 100 m^2/cm^3 and even higher, when pore filling surfactants or molecular templates are used. Water can be removed from wet gels by supercritical drying to produce low-density aerogels or at ambient pressure with various heating protocols. Ambient-pressure drying causes further condensation and collapse of nanopores due to capillary pressure, resulting in densification and internal surface loss. Heat treatment promotes phase changes such as nucleation and growth of crystalline phases, and phase separation, also leading to densification and decreased porosity. Microstructure of mixed oxides is thus influenced in early stages, when small metal-oxide oligomers have a chance for heterocondensation to achieve molecular-scale homogeneity in the wet gel, as well as in later stages, when porosity and homogeneity can be severely modified during drying.

Planar optical waveguides can be prepared by coating silica-titania sols on appropriate substrates to obtain wet gel films, into which diffraction gratings are embossed, followed by further heat treatment in order to achieve required film hardness and stability [7][8]. The final waveguide thickness is on the order of few hundred nanometers. Depending on temperature and duration of drying, the film porosity can be as high as 20%. For standard drying procedures (few hours at 500°) typical porosity was found to be around 15% [9]. With temperatures as high as 900°, the porosity of silica-titania films can be reduced below 1% [10].

In optical waveguide lightmode spectroscopy (OWLS) the effective refractive index of the waveguide for both electric and magnetic modes is measured [11]. The laser light propagates along the waveguide by total internal reflection accompanied by an evanescent wave outside the waveguide surface, so that the optical properties of both the waveguide film and the surrounding environment determine the effective refractive index of the waveguide. Therefore, OWLS is suitable for monitoring of processes leading to changes in the optical density inside and within *ca.* 100 nm of the surface of the optical waveguide. OWLS has been used extensively to study kinetics and equilibria of protein adsorption and structure of adsorbed layers [12–15].

While compact waveguides with negligible porosity were prepared and showed almost negligible response to electrolyte solutions, standard porous waveguides exhibit strong optical response when exposed to electrolyte solutions [16]. This was interpreted as being due to ion adsorption on the internal surface of porous waveguides. To clarify the origin of this optical response, we conducted a series of experiments exposing porous waveguides to NaCl and NaOH solutions, and estimated the resulting changes in polarization densities. Our measurements indicated that the main contribution to the waveguide optical response to electrolyte solutions comes from negatively charged sites at aqueous oxide interface inside electrolyte filled pores of the waveguide.

2. Theoretical Background. – The basic principle of the OWLS is that linearly polarized laser light is coupled by a diffraction grating into the waveguide film, provided that the incoupling condition is fulfilled. The incoupling is a resonance phenomenon that occurs at a certain angle of incidence, when the monochromatic planar electromagnetic wave is guided in the dielectric waveguide by the total internal reflection to the detector. Effective refractive index N of the waveguide can be calculated from the incoupling condition for the first order diffraction $N = n_{\mathrm{air}} \sin \alpha + \lambda/\Lambda$, where Λ is the grating period, λ is the laser beam wavelength, and α is the incoupling angle [11]. The phase change undergone by the wave on the round trip across the waveguide (it means reflection at the F,S interface, across F to F,C interface, reflection at the F,C interface and back to F,S) is equal to an integral multiple of 2π. Under this condition, we obtain the zeroth-order mode equation for the electromagnetic wave propagating indefinitely along an asymmetric planar waveguide:

$$0 = 2k_{\mathrm{o}} t_{\mathrm{F}} \sqrt{n_{\mathrm{F}}^2 - N^2} + \Phi_{\mathrm{F,S}} + \Phi_{\mathrm{F,C}} \qquad (1)$$

The mode equation (*Eqn. 1*) gives the relation between the measured effective refractive index N and optogeometric parameters of the composite waveguide. Here $\Phi_{\mathrm{F,S}}$, $\Phi_{\mathrm{F,C}}$ denote the phase shifts upon reflection at the interfaces, $k_0 = 2\pi/\lambda$ is the wave number of the free space, t_{F} is the thickness, and n_{F} is the refractive index of the waveguide film.

If the refractive index of the waveguide film or its surrounding environment changes, for example, due to adsorption of molecules, deposition of particles, or surface reactions resulting in different polarizability of surface atoms and molecules, it affects the phase shift of the electromagnetic wave from the solid-liquid interface. Experimentally measured resonance is then detected under a different angle of incidence. Upon assumption that interfaces between the layers are abrupt and the layers are homogeneous and isotropic, the mode equation (*Eqn. 1*) can be written in terms of the waveguide-film thickness and the refractive index [11]:

$$0 = 2k_0 t_F \sqrt{n_F^2 - N^2} - \arctan\left[\left(\frac{n_F}{n_S}\right)^{2\rho}\left(\frac{N^2 - n_S^2}{n_F^2 - N^2}\right)^{1/2}\right] - \arctan\left[\left(\frac{n_F}{n_C}\right)^{2\rho}\left(\frac{N^2 - n_C^2}{n_F^2 - N^2}\right)^{1/2}\right] \quad (2)$$

where $\rho = 0$ for the transverse electric mode TE and $\rho = 1$ for the transverse magnetic mode TM. We use the *Eqn. 2* to calculate properties of the waveguide exposed to pure water and electrolyte solutions. When effective refractive indices N_{TE} or N_{TM} are measured and refractive indices n_S and n_C of media surrounding the waveguide film are known, one can calculate the refractive index of the waveguide film n_F and its thickness t_F. Dependence of n_C on electrolyte concentration is available for common electrolytes [17].

Refractive index of the waveguide film can be changed due to adsorbed ions or charged groups at aqueous solid interface in the pores. The relation between the refractive index n of a multicomponent system and the effective electronic polarizabilities of its components is given by the *Lorenz-Lorentz* equation [18]:

$$\frac{4\pi}{3}\sum_{i=1}^{n} \alpha_i c_i = \frac{n^2 - 1}{n^2 + 2} \quad (3)$$

where α_i and c_i denote the electronic polarizability (in units of m^3) and the number concentration (in units of m^{-3}) of the component *i*.

The electronic polarizability indicates how easy the electron cloud is deformed by an applied electrostatic field. Ions in aqueous solutions have different electronic polarizability from those in the gas phase or in an ionic crystal. Water molecules in the ionic hydration shell have more stable spatial orientation compared to the bulk, due to strong electrostatic charge–dipole interaction, and they screen the electronic polarizability of ions. The polarizabilities of hydrated ions can be found in terms of the effective electronic polarizabilities [19]. Experimental observations showed that the electronic polarizability of cations is about one order of magnitude smaller than the electronic polarizability of anions for similar atom sizes. This is because the cloud of electrons surrounding a cation is smaller and, therefore, less deformable by an applied external electric field. For the same reason, bigger cations have higher polarizability than the smaller ones with the same charge.

3. Experimental. – Experiments were performed with the *OWLS 110* instrument and *OW 2400c* waveguides supplied by *Micro Vacuum Ltd.*, Budapest, Hungary. Waveguides deposited on a glass substrate were films *ca.* 175-nm thick, made of mixed oxide titania-silica (Ti/Si 3:1), and coated with a thin layer (10 nm) of SiO_2. Parameters of the waveguides provided by the manufacturer were: refractive index of the glass substrate 1.5258, grating period $\Lambda = 416.7$ nm, wavelength of laser light $\lambda = 632.8$ nm.

Waveguide treatment procedure was as follows: the waveguide was exposed to the HCl soln. at pH 2.5. Then, it was exposed to deionized doubly distilled H_2O in order to stabilize the optical signal. When the optical response was constant over several hours, the surface was taken to be in the reference state. A set of experiments was then performed by bringing the waveguide into contact with a series of electrolyte solns. of increasing ionic strength and/or pH. Each soln. was flowed through a cuvette attached to the waveguide surface, and the optical signal was recorded until a steady state was achieved, and then the next soln. was introduced. After each set of experiments, the waveguide was treated with the HCl soln., until the same response was obtained as before the experiment, and then the surface was left exposed to pure H_2O for the next experiment.

Experiments were carried out at 298 K under N_2 atmosphere. The ionic strength of aq. solns. was varied by adding NaCl or NaOH. NaOH Solns. were stored in plastic bottles under N_2 atmosphere to avoid the adsorption of CO_2 from the ambient air. A peristaltic pump was used to push solns. through the cuvette attached to the waveguide surface. The flow through the cuvette was in the laminar regime with the flow rate 1 ml/min. pH was monitored by *Sure-Flow ROSS* combination pH electrode by *ORION*, type *8172BN*. The electrode was calibrated before each experiment. Refractive index of bulk solns. at r.t. was measured by the differential refractometer *Merck-La Chrome RI* detector, type *L-7490*.

Two sets of experiments are reported here. The first set of experiments was performed with a series of NaCl concentrations between 10^{-6} and 10^{-1} M without pH adjustment (measured pH values were between 6.3 and 7.0). The second set of experiments was conducted with a series of solns. with pH values between 6 and 10 at a constant ionic strength due to 0.1M NaCl.

4. Results and Discussion. – Porous waveguides exposed to pure H_2O were equilibrated for *ca.* 1 d to eliminate observable downward drift of their refractive index, which is likely due to washing and possibly minor hydrolysis and dissolution of oxides constituting the waveguide. When a waveguide equilibrated with pure H_2O was exposed to electrolyte solutions, the observed refractive index increased and gradually reached a steady value. Characteristic time for reaching steady-state optical response varied from *ca.* 100 min at lowest ionic strengths ($< 10^{-4}$ M) to 1–2 min at 0.1M NaCl. In *Fig. 1*, we show the measured steady-state refractive-index increment as a function of NaCl concentration in liquid phase in contact with the waveguide. These results for the silica-coated waveguide are in a very good agreement with data obtained for uncoated waveguides [16]. However, characteristic times for reaching steady-state optical response in uncoated waveguides were *ca.* 10 min, *i.e.*, by one order of magnitude faster than for silica coated waveguides used in this study.

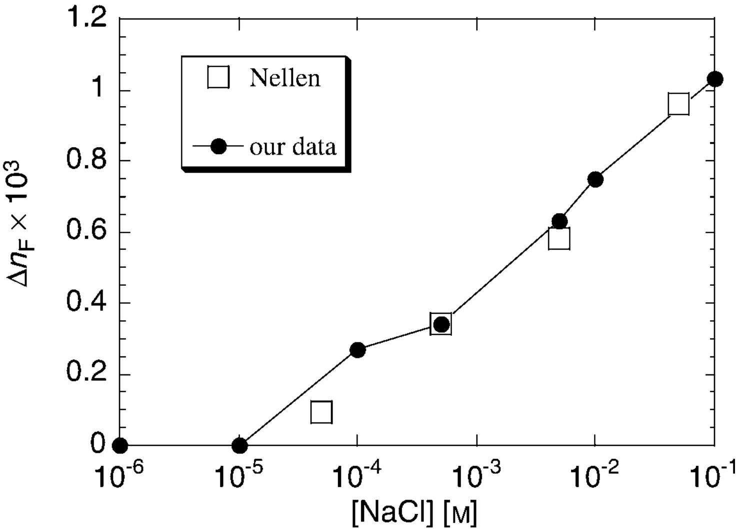

Fig. 1. *Measured increment in film refractive index* vs. *NaCl concentration at neutral pH*

Next, we compare measured waveguide refractive-index increments with those corresponding to the bulk NaCl solution filling the waveguide pores. With typical values of the waveguide porosity $\phi = 0.15$ [9], the refractive index of waveguide equilibrated with pure H_2O $n_F = 1.77$, and $[NaCl] = 1$ mM ($\Delta n_C = 1.0 \times 10^{-6}$ compared to pure H_2O), we get the refractive-index increment $\Delta n_F = \phi \Delta n_C = 1.5 \times 10^{-7}$, assuming that the bulk NaCl solution replaced pure H_2O in the whole pore volume of the waveguide. The refractive-index increment calculated is by more than three orders of magnitude smaller than the measured value of the refractive index increment 4×10^{-4} for 1 mM NaCl (*Fig. 1*) and below the resolution of the current instrument. Therefore, the increase observed in the refractive index cannot be explained by NaCl uptake in waveguide pores alone. Thus, we postulate that the observed optical response is due to changes induced by the electrolyte solution at the internal aqueous oxide interface in waveguide pores.

It is well-known that proton dissociation equilibria at aqueous oxide surfaces are shifted towards dissociation with increasing solution ionic strength. At pH (6.3 – 7.0) values in the first set of experiments, both silica and titania are negatively charged, and their surface charge increases with concentration of an indifferent electrolyte, such as NaCl [20]. For example, the measured values of surface charge on both silica and titania for 0.1M NaCl and pH 7 were found to be around 5×10^{-2} C/m^2 [21]. Note, however, that the isoelectric point of silica is 2 – 3, while the isoelectric point of titania is 6.0. Now let us use the *Lorenz-Lorentz* equation (*Eqn. 3*) to estimate the refractive-index increment due to negatively charged oxygen sites at internal surface of the porous waveguide. Let us take a typical value for the effective (hydrated) polarizability difference between the oxo-anion and the neutral molecule, *e.g.*, $\Delta\alpha_i = \alpha_{H_2O} - \alpha_{OH^-} = 0.9 \times 10^{-30}$ m^3, the internal surface area of the waveguide film to be 25 times larger than the outer film surface (corresponding to the film thickness 175 nm and a reasonable internal surface area 1.5×10^8 m^2/m^3) and the surface charge density 5×10^{-2} C/m^2 (*i.e.*, 5×10^{-7} mol/m^2 assuming charge -1 per anion). Then, the anion concentration in the waveguide is $c_i = 2 \times 10^{25}$/m^3, and, from *Eqn. 3*, we get the polarization density increment $(4\pi/3)c_i\ \Delta\alpha_i = 2 \times 10^{-4}$, which is of the same order of magnitude as the measured optical response $\Delta\left((n_F^2 - 1)/(n_F^2 + 2)\right) = 6 \times 10^{-4}$ for 0.1M NaCl and pH 7. It is, therefore, quite reasonable to suggest that the waveguide optical response comes from negatively charged internal pore surface of the waveguide.

When the waveguide equilibrated with NaCl solution is exposed to pure H_2O again, only a partial recovery of the refractive index is observed within few min, followed by a very slow further decrease. Thus, the complete removal of NaCl from the waveguide is much slower than its entry at near neutral pH of pure H_2O. The observed behavior of NaCl uptake in waveguide pores indicates that most of NaCl that diffused in is essentially immobilized at $pH > 6$. Although both titania and silica are negatively charged at $pH > 6$, and more so with increasing ionic strength, specific sodium binding is negligible at this pH for silica [22] and titania [23] as well. However, the diffusive mobility of ions in nanopores can be hindered due to surface charge at pore walls.

To achieve a complete removal of NaCl from the waveguide, we used the acid treatment with HCl at pH 2.5. During the acid treatment, the waveguide refractive index decreased rapidly to values equal or lower than those measured at the previous equilibration with pure H_2O. This indicates that NaCl was removed from the waveguide pores, its transport being likely facilitated by neutralization of negative surface charge on pore walls. After the HCl treatment, the waveguides were exposed to pure H_2O, and there was no significant difference in the optical response between HCl solutions of pH

2.5 and pure H_2O, even though both media differ slightly in the refractive index. This means that there is a negligible change of the polarization density of the waveguide exposed to pure H_2O compared to that exposed to HCl solution at pH 2.5.

In the second set of experiments at the higher ionic strength (0.1M NaCl) and a range of pH values up to 10, we found a stronger optical response than at low ionic strength and pH, consistent with charging behavior of the aqueous oxide interface. Two important differences were observed compared to experiments at lower ionic strengths. Characteristic time of achieving a steady-state optical response was shorter (*ca.* 1–2 min), and the optical response was nearly reversible on the same timescale. Similar qualitative observations were previously made on plain titania-silica waveguides exposed to a phosphate buffer [16], although, in their case, a substantial variation in the film refractive index was also observed when pH was changed between 3 and 6.

Both of these observations can be explained by considering the screening effect of the background electrolyte on the electrical double layer at charged pore walls, which would reduce electrostatic repulsion between pore walls and diffusing ions, increasing their mobility. Since measurements of surface charging for both titania and silica surfaces as a function of pH in 0.1M NaCl solutions are available, we can compare these data to the optical response observed under the same conditions, as measured in the second set of experiments. In *Fig. 2*, we plot the polarization-density increment calculated from the measured film refractive index as a function of solution pH. From the analysis above, we expect that this quantity is proportional to the surface-charge density within the porous waveguide, composed of mixed amorphous silica and microcrystalline anatase titania [24]. In *Fig. 3*, we show a collection of experimental data on surface charges on titania (anatase) and silica (amorphous) [21]. We see that the observed optical response trend is more similar to that observed for titania (*Fig. 3,a*) than that for silica (*Fig. 3,b*).

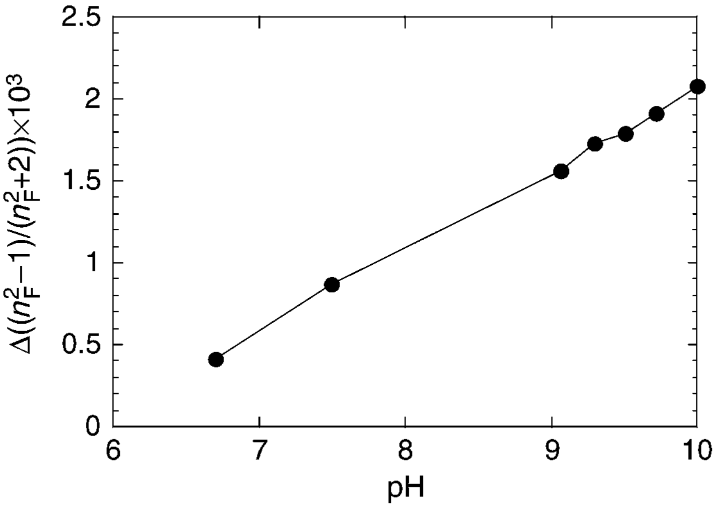

Fig. 2. *Measured increment in polarization density* vs. *pH for 0.1M NaCl solutions*

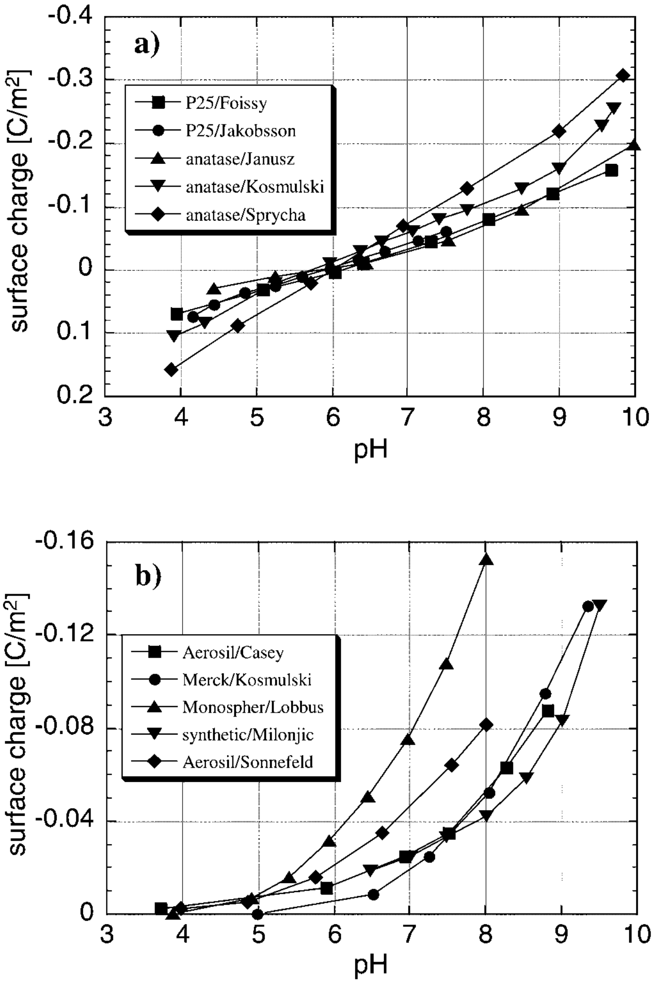

Fig. 3. *Literature data on oxide surface charge* vs. *pH for 0.1*M *NaCl solutions: a) titania* (anatase), *b) silica* (amorphous) [21]

Finally, we estimate the effective diffusion coefficient for NaOH inside the porous waveguide, using the observed characteristic time 1 min and the characteristic length 175 nm equal to the waveguide-film thickness, we obtain $D_{\mathrm{eff}} = \mathrm{length}^2/\mathrm{time} = 5 \times 10^{-12}$ cm^2/s. This value is by *ca.* five orders of magnitude smaller than the expected effective diffusion coefficient based on infinity dilution diffusivity of NaOH in H_2O ($D = 1 \times 10^{-6}$ cm^2/s) and accounting for pore volume fraction and tortuosity. Thus, even at the ionic strength 0.1M, the diffusion of small electrolytes inside the waveguide pores is severely hindered, with diffusivities by *ca.* 10^5 times smaller than those in H_2O.

5. Conclusions. – We used OWLS to study optical response of porous titania-silica waveguides exposed to electrolyte solutions. The observed optical response is consistent with aqueous oxide surface charging and can be due to either the polarizability of the negatively charged surface sites or the polarizability of counterions in the electrical double layer. However, the calculated contribution to the polarization density from the sodium salt present in waveguide pores was found to be by several orders of magnitude smaller that the measured quantities. Therefore, the influence of Na^+ cations is not a dominant factor determining the value of the measured optical response signals. We conclude that the main contribution to the polarization density comes from highly polarizable negatively charged oxygens, corresponding to the charge density at the internal surface of porous waveguides.

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