A method for obtaining *in situ* external reflectance infrared spectra in strongly acidic solutions using fluorite windows

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ABSTRACT

We report a simple method that allows to obtain external reflectance infrared spectra in strongly acidic solutions using a fluorite window without damaging it. The method is demonstrated by measuring the infrared spectra of carbon monoxide adsorbed on a nickel electrode in 7.5% and 28% aqueous HCl solutions.

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1. Introduction

Bewick's seminal work in the 80s [1] opened up an ever expanding use of external reflectance infrared spectroscopy for the chemical and structural characterization of the electrode–electrolyte interface at the molecular level [2]. Typically, fluorite prisms bevelled at 60° are used as windows against which the electrode is pressed forming a very thin (1–10 μm) electrolyte layer through which the infrared radiation reaches the electrode surface and, after reflection from the electrode surface, travels back from it. Light enters and exits the prism at normal incidence, thus minimizing the energy losses due to reflection, and reaches the fluorite–electrolyte interface at an angle of incidence of 60°, which coincides with the critical angle at 1000 cm^{−1}, the frequency within the usable fluorite spectral range at which the refraction index of water is minimum. Thus, the angle of incidence at the fluorite–electrolyte interface is kept just below the critical angle, and the angle of incidence at the electrode–electrolyte interface is as high as possible (around 73° at 2000 cm^{−1}). Flat fluorite windows are also sometimes used, but in this case the infrared radiation must enter the window with an angle of incidence as close to the Brewster angle as possible. At the Brewster angle (54.5°), the angle of incidence at the electrode–electrolyte interface would be, at 1000 cm^{−1}, ca. 43°. This can be increased to ca. 51° if the infrared

radiation enters the fluorite window at 68°, but then a larger amount of radiation would be reflected, and, hence, lost, at the air–window interface. In any case, the angle of incidence at the electrode–electrolyte interface is clearly smaller than with a fluorite prism, producing a smaller electric field, and therefore a smaller sensitivity for adsorbed species.

Although fluorite is soluble in acids, it can withstand the solutions typically used in fundamental research, which rarely go below pH 0. However, fluorite readily dissolves in strongly acidic solutions, this making the chemical and structural characterization by *in situ* infrared spectroscopy of the electrode–electrolyte interface, under conditions similar to those used in technologically relevant processes, virtually impossible. Silicon windows could be used instead, but in this case prisms bevelled at 20° should be used, to avoid total reflection at the silicon–aqueous solution interface. Although an *ad hoc* home-made reflection accessory could be designed, this is not accessible to all laboratories, and with most of the commercial reflection accessories it is not possible to reach an incidence angle lower than 30°. With a flat Si window, the best angle of incidence at the air–Si interface is again the Brewster angle (73.4°), with which the angle of incidence at the electrode–electrolyte interface would be ca. 53° at 1000 cm^{−1}, resulting, as with a flat fluorite window, in a loss of sensitivity.

In the following we report a very simple method that has allowed us to obtain infrared spectra of CO chemisorbed on Ni electrodes in concentrated HCl aqueous solutions using fluorite windows.

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Fig. 1. Background spectra of the infrared radiation reflected from a nickel disk immersed in water and pressed against a prismatic fluorite window (black line), and against a prismatic fluorite window protected by self-adhesive polypropylene tape (red line).

2. Experimental

The working electrode was a Ni disk, 12 mm in diameter, cut from a 1-mm thick sheet of 99.99% Ni from Advent, polished with alumina of 5, 0.3, and 0.05 μm and sonicated in Milli-Q water.

A platinum wire was used as a counter electrode, and a freshly prepared reversible hydrogen electrode (RHE), to which all the potentials in the text are referred, was used as reference.

Saturated CO adlayers were formed potentiostatically at $E = -0.3$ V by saturating the working solutions with CO. The working solutions (7.5% and 28% HCl) were prepared from concentrated HCl and Milli-Q water. Nitrogen (N50) and carbon monoxide (N47, aluminium alloy cylinders) were supplied by Air Liquide.

FT-IRS experiments were carried out in a Perkin-Elmer FT-IR spectrophotometer, model 1725-X, using a CaF_2 prismatic window bevelled at 60° . Reflectance spectra were calculated as $\frac{\Delta R}{R} = \frac{R_s}{R_{\text{ref}}} - 1$, where R_s and R_{ref} correspond to the single-beam reflectance spectrum at the sample and reference potentials, respectively, each single spectrum consisting of 100 interferograms with a resolution of 8 cm^{-1} . Positive bands indicate absorption by a species present at the reference potential and absent at the sample potential, while negative bands indicate IR absorption by a species present at the sample potential and absent at the reference potential. Bipolar bands correspond to species adsorbed on the electrode surface at both the reference and sample potentials, but whose frequency changes with potential. In order to avoid dissolution of the fluorite window by the strongly acidic solutions used, a thin film (ca. $50\text{ }\mu\text{m}$) of commercial self-adhesive film, composed of polypropylene (atactic, according to its transmission infrared spectrum) and an acrylic adhesive, was adhered to the surface of the prism facing the electrolyte, taking care not to leave any air bubble between the fluorite surface and the plastic film.

3. Results

Recently a method has been proposed [3] that, by combining the availability of simple processes for the deposition of thin metal films on Si and the stability of Si in acidic electrolytes with the good transmittance of ZnSe windows below 1000 cm^{-1} , allows to obtain IR spectra in the highly advantageous ATR configuration. The method consisted in placing a thin Si wafer on top of the ZnSe

Fig. 2. Spectra of CO chemisorbed on a Ni electrode in CO-saturated 7.5% HCl (black line) and in 28% HCl. CO was adsorbed at -0.30 V. The reference spectrum was recorded at -0.30 V in the 7.5% HCl solution and at -0.20 V in the 28% HCl solution. The sample potential was -0.10 V in both cases.

prism used as ATR window, and was later improved by sandwiching an ultrathin water layer between the Si wafer and the ZnSe prism [4]. This ultrathin water layer acts as an effective optical coupler, minimizing the strict requirements of surface flatness and roughness necessary for optically coupling two solids. We tried to adapt this procedure to strongly acidic solutions, by substituting a thin polystyrene or polyethylene film for the Si film. However, with this experimental configuration the water thickness was not homogeneous and changed during the time needed for recording an infrared spectrum, provoking interference patterns that strongly distorted the spectra. Fortunately, we achieved excellent results by substituting both the Si wafer and the water layer by a self-adhesive plastic film, the adhesive material acting as an efficient optical coupler.

Fig. 1 shows background spectra (energy, in arbitrary units, vs. frequency) of the infrared light reflected from a Ni disk immersed in Milli-Q water, and pressed against the fluorite window. The black line is the energy curve recorded with a naked fluorite window, while the red line corresponds to the energy curve recorded with a fluorite window covered by a thin self-adhesive polypropylene film. As can be observed, below 2700 cm^{-1} and above 1500 cm^{-1} the transmittance of the fluorite window is nearly unaffected by the presence of the plastic film, except for the band at 1730 cm^{-1} , due to the carboxylic group of the acrylic adhesive. The characteristic bands of polypropylene at 1457 and 1375 cm^{-1} can be clearly observed in the corresponding spectrum (Fig. 1, red¹ line).

In order to check the method, we measured the infrared spectrum of CO adsorbed on Ni electrodes in concentrated HCl solutions. Fig. 2 shows potential-difference spectra recorded in CO-saturated 7.5% (black line) and 28% (red line) HCl. The spectra were recorded after bubbling CO through the solution for 20 min at $E = -0.3$ V. Due to the large uncompensated resistance inherent to the thin layer configuration, and to the huge currents flowing at positive potentials in these strongly acidic solutions, it was not possible to oxidize the adsorbed carbon monoxide, and bipolar

¹ For interpretation of color in Figs. 1 and 2, the reader is referred to the web version of this article.

bands, due to the increase in the CO stretching frequency with potential, were always obtained.

The adsorption of CO on nickel electrodes at pH 3–14 has been studied previously [5,6]. It was found that CO adsorbs on Ni both in the linear (CO_L) and the bridge (CO_B) forms, the relative amount of linear CO increasing with decreasing pH: at pH 14 the band corresponding to CO_L was clearly smaller than that corresponding to CO_B , while at pH 3 the band of CO_L was clearly larger than that of CO_B . The results in Fig. 2 are consistent with those reported in [5,6], with a bipolar band of CO_L around 2050 cm^{-1} in 7.5% HCl and around 2060 cm^{-1} in 28% HCl, and a smaller, also bipolar, band of CO_B around 1905 cm^{-1} in 7.5% HCl and around 1920 cm^{-1} in 28% HCl. The CO_L band appears at clearly higher frequencies in 28% HCl than in 7.5% HCl, this being consistent with the pH independence of the CO stretching frequency at a given potential vs. a pH-independent reference electrode reported in [6], were it was attributed to the exclusion by chemisorbed CO of water and its ions from the metal surface.

4. Conclusions

We report here a new method that allows the measurement of infrared spectra in the external reflectance configuration in

strongly acidic solutions using fluorite windows. The method was demonstrated by recording the infrared spectra of CO chemisorbed on Ni electrodes in 7.5% and 28% HCl. Although with the adhesive tape used only the spectral region above $1490\text{--}1500\text{ cm}^{-1}$ was accessible, it should be possible to access a wider spectral range by using different combinations of plastic films and adhesives.

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