



Influence of water on the hydrogen evolution reaction on a gold electrode in acetonitrile solution



Isis Ledezma-Yanez, Marc T.M. Koper*

Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

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ABSTRACT

Here we discuss the importance of water in proton solvation for the hydrogen evolution on polycrystalline gold microelectrodes. We perform cyclic voltammetry in acetonitrile electrolyte, in presence and absence of added amounts of water, with the interfacial movement of water and ions monitored by means of in situ Fourier Transform InfraRed (FTIR) spectroscopy. Our results show that trace amounts of water accumulate at the gold-acetonitrile interface. In the absence of protons (from a proton source), this water leaves the interface with more negative potential. In the presence of protons, we observe preferential solvation of protons by water, and water accumulates at the electrode surface under conditions of hydrogen evolution. Tafel plot analysis shows that the hydrogen evolution on gold in acetonitrile presents the same rate-determining step as for polycrystalline platinum, implying that the first electron transfer to yield adsorbed hydrogen is the rate-determining step of the reaction.

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1. Introduction

Hydrogen evolution in non-aqueous solvents has been subject of study for many years, with a general focus on the dependence of the catalytic activity on the nature of the catalyst and the proton donor [1–6]. More recently, the influence of small or even trace amounts of water in acetonitrile solutions has been studied for a variety of electrochemical reduction or protonation reactions, such as hydrogen evolution, oxygen reduction, and carbon dioxide reduction [7–11]. In our previous work on hydrogen oxidation and proton reduction on the benchmark catalyst, i.e. platinum [9], we showed by in situ Fourier-Transform Infrared (FTIR) spectroscopic analysis that the hydrogen oxidation and evolution (HOR/HER) in acetonitrile is assisted by a preferential solvation of protons in water. The HOR/HER appears to be so sensitive to the presence of water that even trace amounts influence the process. It would be important to characterize the role of water for non-ideal catalytic behavior, as it is the case with polycrystalline gold electrodes, on which the HOR does not proceed. An older study on the HER on platinum and gold can be found in literature [12], focusing on the solvation of two different acids (HCl and HPic) in acetonitrile. Their main findings pointed out the homoconjugation effect between the acid and the acetonitrile, due to incomplete dissociation of the acids, as well as the electroadsorption of the solvent on the electrode surface, leading to irreversible behavior. However, the influence of water was not taken into account.

Here we present a spectroelectrochemical study, combining cyclic voltammetry and FTIR experiments, of the HER in acetonitrile with 0.1 M tetrabutylammonium electrolyte, in presence and absence of 10 mM of perchloric acid as proton donor, under argon and hydrogen atmosphere. The experiments were also performed in presence of added water (50 mM), to evaluate the importance of the water-proton and water-electrode interactions. The cyclic voltammetry and FTIR spectroscopy show that the HER on gold is mediated by the presence of water due to a preferential solvation of protons, in a similar fashion to what has been reported for platinum electrodes [9]. This behavior appears to play an important role already at very low water concentrations.

2. Materials and Methods

Prior to experiments, the glassware was rinsed with water (Milipore® MiliQ; resistivity > 18.2 MΩ·cm), rinsed with acetone (Sigma-Aldrich) and placed in the oven overnight at 120 °C. Acetonitrile (Anhydrous 99.8%, from Sigma-Aldrich) with tetrabutylammonium perchlorate (99.0% from Sigma-Aldrich) were used as received for preparing the solutions. Ferrocenium hexafluorophosphate (97%, from Sigma-Aldrich) and ferrocene (99%, from Alfa Aesar) were used for preparing an equimolar solution to calibrate the equilibrium potential of the home-made Ag/AgClO₄ (97% from Sigma-Aldrich) reference electrode (RE). Perchloric acid (70%, Suprapur from Merck) was used as a proton source. The solutions were purged with argon (purity grade 6.0). For the experiments under hydrogen atmosphere we used a constant hydrogen flux (purity grade 5.6). All solutions used in this work are considered “wet”, since we did not treat the reactants prior to use.

* Corresponding author.

E-mail address: m.koper@chem.leidenuniv.nl (M.T.M. Koper).

Karl Fischer (KF) titration was performed for the several acetonitrile solutions used, in presence of Ar or H₂. The water content of the different solutions can be found in Table 1:

Addition of 10 mM HClO₄ would lead to an increase of the water concentration by ca. 100 ppm, calculated directly from the nominal water concentration from the mineral acid (an acetonitrile solution of 0.1 M HClO₄ contains 10,100 ppm of water). This implies that the water content in the acetonitrile solutions in presence of TBAClO₄ and 10 mM of HClO₄ is ca. 350 ppm.

Cyclic voltammetry was measured in a one-compartment, three-electrode cell connected to an Ivium potentiostat/galvanostat (IviumStat). The working electrode (WE) consisted of a gold wire, with a diameter of 120 μm and a real surface area of $(4.2 \pm 0.2) \times 10^{-2}$ cm² (obtained by measuring the area of the reduction peak from the gold oxides in aqueous electrolyte), assembled into a glass stem. The gold microelectrode was flame annealed and rinsed with water and acetone before each measurement. We used a gold spiral as the counter electrode (CE) and a Ag/AgClO₄ electrode in acetonitrile as the reference electrode (RE). A 10 μF capacitor was connected between the RE and a platinum wire immersed in the solution, as a noise filter. The equilibrium potential of the redox couple Fc⁰/Fc⁺ was calculated as the half wave potential using cyclic voltammetry with a measured value of 0.038 V vs. Ag/AgClO₄.

The Fourier Transform Infra-Red Spectroscopy measurements were performed in a three electrode cell coupled to a CaF₂ prism slanted at 60°, and connected to a Bruker Vertex80V IR spectrophotometer. A gold disk was mechanically polished with alumina of three different mesh (Alfa-Aesar), rinsed in an ultrasonic bath, flame-annealed and settled in the cell in a thin layer configuration, by pressing it against the prism. This procedure should ensure that the gold electrode is free from residual oxides at the start of the experiment. The CE was a gold wire and the RE was the Ag/AgClO₄. Hundred interferograms were averaged for each spectrum, with a resolution of 8 cm⁻¹. The transmission spectra used for the elucidation of bands in “dry” electrolyte were reported previously [9], whereas the transmission spectra for the electrolyte solutions with added water were recorded using a SeZn window with an incident angle of 60°. One hundred scans were collected with a resolution of 8 cm⁻¹ using p-polarized light. The reference spectrum was acquired from pure acetonitrile. All spectra in this work are reported as absorbance spectra, according to the approximation $A \approx \Delta R/R_0$ where R and R_0 are the reflectance corresponding to the single spectra obtained for the sample potential and the reference potential at their respective potentials. The interpretation of the bands is as follows: bands pointing upwards correspond to the formation of species at the surface at the sample potential with respect to the reference potential, and are called positive bands, while bands pointing downwards indicate the depletion of species from the electrode surface and are called negative bands.

3. Results

3.1. Characterization of the Hydrogen Evolution on Polycrystalline Gold in Acetonitrile by Cyclic Voltammetry

Fig. 1a and b depict the voltammograms collected for a polycrystalline gold microelectrode in acetonitrile solutions, containing 0.1 M of tetrabutylammonium perchlorate (TBAP) in the absence and presence of 50 mM of water, respectively. We present the second and last scan

out of 200 voltammograms, recorded at a scan rate of 500 mV·s⁻¹. The dashed lines correspond to electrolytes under Ar-saturated conditions, whereas the solid lines represent the voltammograms for the H₂-saturated solutions. For the electrolyte with argon (Fig. 1a) we observe a reduction current at ca. $-0.8 V_{Ag/Ag+}$ and an adsorption/desorption process at ca. $0.5 V_{Ag/Ag+}$. These peaks decrease and stabilize after the sixth scan (not shown), reaching the size and shape presented in the 200th scan. In the same subfigure, it is shown that the main difference in the second and last scan for the electrolyte in presence of H₂ is a smaller current corresponding to the peak at ca. $0.5 V_{Ag/Ag+}$, suggesting that this process changes under H₂ saturation. This effect is ascribed to a higher water availability at the electrode surface, as suggested by the blanks obtained in presence of added water, shown in Fig. 1b, top panel. This confirms the result from the KF titration (see Table 1) that bubbling H₂ brings (a small amount of) water into the cell. While we cannot totally rule any reducing effect of H₂, we believe that the main effect of bubbling H₂ is the introduction of small amounts of water. The second scans recorded in presence of argon or hydrogen also show the reduction peak at $-0.8 V_{Ag/Ag+}$ as well as the oxidation-reduction peaks at ca. $0.5 V_{Ag/Ag+}$, but with a smaller current compared to the voltammograms observed in the electrolyte without added water. In the 200th scan for the water-containing acetonitrile, in presence of argon or hydrogen, we observe a redox peak at $0.84 V_{Ag/Ag+}$, presumably corresponding to the formation of gold (hydr)oxides [13]. These observations suggest that the gold-electrolyte interface is affected by the presence of water, and leads to oxide formation in the presence of considerable amounts of water. Our results also show that the hydrogen oxidation does not proceed on gold under the conditions studied.

In Fig. 1a, bottom panel, we present the HER current observed with the addition of 10 mM of HClO₄, in presence and absence of hydrogen. The voltammograms are similar in current and shape, with an onset for proton reduction at ca. $-0.50 V_{Ag/Ag+}$. The presence or absence of hydrogen made no observable difference in the HER. Addition of 50 mM of water (Fig. 1b, bottom panel) produced no significant changes in current or other features compared to the voltammograms obtained from the electrolytes without added water.

Finally, Fig. 1c shows the last scan out of 50 voltammograms recorded in a much wider potential window at 50 mV·s⁻¹, for the electrolyte in presence of added water and argon. No water reduction is observed; only solvent decomposition at ca. $-2.9 V_{Ag/Ag+}$. A small oxidation peak is observed at ca. $-0.35 V_{Ag/Ag+}$, probably related to the electrolyte adsorption at the electrode surface, as consequence of the lower scan rate used. This large potential window of (apparent) electrolyte stability is in agreement with what was previously reported by Gerischer and Wagner [14].

3.2. Evaluation of the Water Effect on the Hydrogen Evolution on Polycrystalline Gold Using Fourier-Transform InfraRed Spectroscopy

Fourier-Transform InfraRed (FTIR) spectroscopy was performed at a series of fixed potentials, for all the systems characterized in the previous section by cyclic voltammetry. The transmission spectra for these acetonitrile solutions have been discussed in our previous work [9]; therefore, the interpretation of the main features shown in this work are based on the aforementioned study, in agreement with earlier reports from the literature [15–17].

We will discuss the features which are sensitive to the presence of added water and hydrogen; namely, the acetonitrile bands, the water bands and the bands attributed to the supporting electrolyte, TBAP, i.e. TBA⁺ cations and ClO₄⁻ anions. The C–N bending and stretching modes from acetonitrile are observed in the range 2260–2340 cm⁻¹, and the C–H modes in the range 2900–3000 cm⁻¹. We note that the C–H modes are more intense in the presence of the electrolyte TBAP, due to the butyl chains present in the cation [9]. The presence of water is characterized by bands in the O–H stretching region between 3100 and 3750 cm⁻¹, and by the bending modes in the 1500–

Table 1
Water content (in ppm) for different acetonitrile solutions determined from Karl Fischer titration.

Solution	H ₂ O content (ppm)
MeCN (Ar)	54 ± 8
MeCN + TBAClO ₄ (Ar)	153 ± 14
MeCN + TBAClO ₄ (H ₂)	244 ± 41

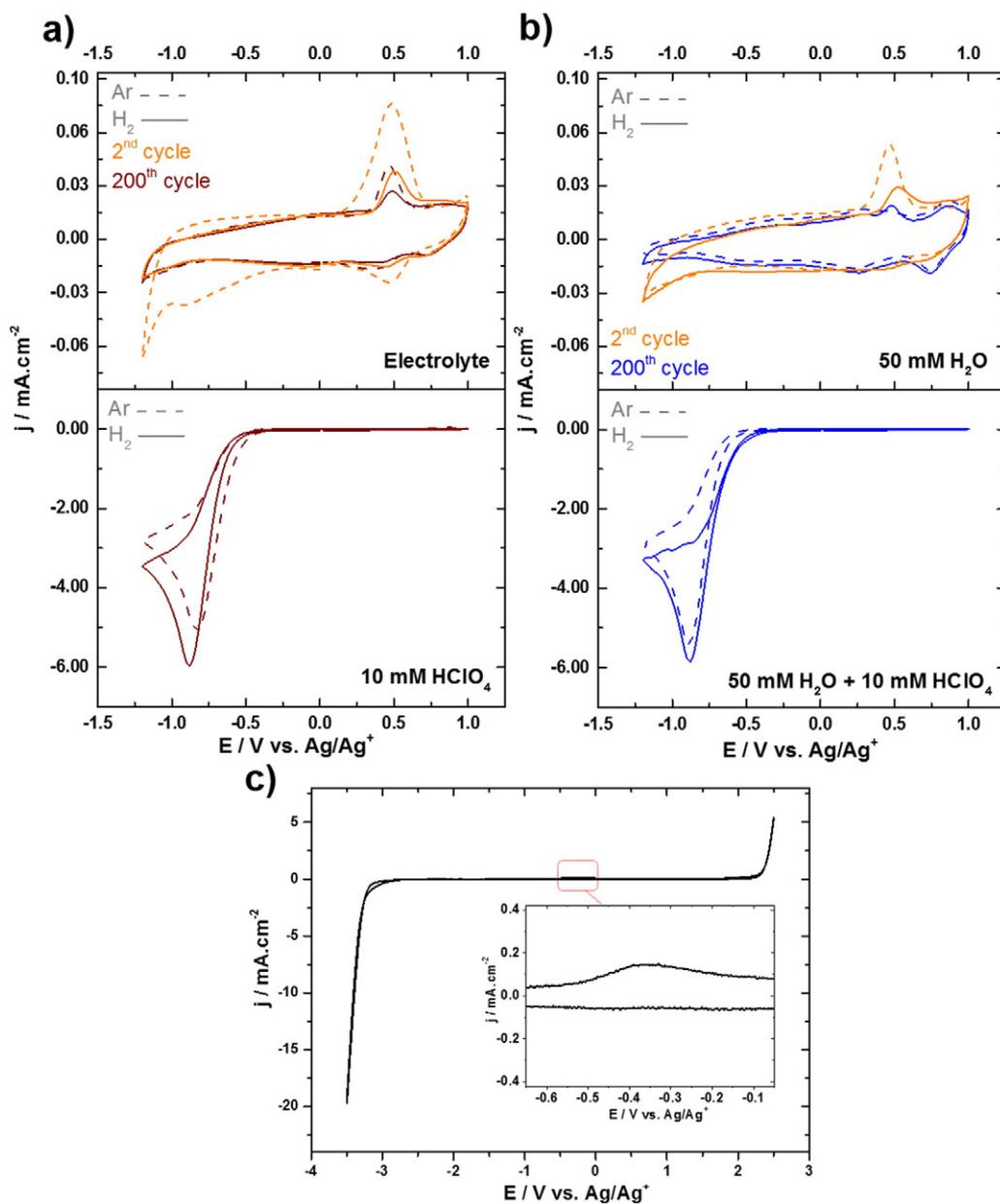


Fig. 1. Cyclic voltammograms for a polycrystalline gold microelectrode in acetonitrile, containing 0.1 M TBAClO₄ as supporting electrolyte, with and without 10 mM of HClO₄. a) Using acetonitrile and supporting electrolyte as received, scan rate: 500 mV/s; b) After adding 50 mM of water, scan rate: 500 mV/s; c) In a wider working window in presence of 50 mM of water and argon saturation, scan rate: 50 mV·s⁻¹; inset: zoom in of the potential window -0.7 to -0.2 V_{Ag/Ag⁺}.

1650 cm⁻¹ range. The perchlorate ion presents a sharp band around 1130 cm⁻¹, from the Cl—O stretching mode. This vibration of the perchlorate anion has been reported by Barthel et al. [15] to be susceptible to the formation of ion pairs in acetonitrile solutions, as manifested by the presence of low- and/or high-frequency shoulders.

The spectra were acquired from positive towards negative potentials (top to bottom in each figure), and the reference spectrum was recorded at 0 V_{Ag/Ag⁺}. The positive bands are related to the formation or accumulation of species at or near the electrode surface, whereas the negative bands indicate the depletion of species out of the double layer region.

Fig. 2 shows the spectra collected for a gold electrode in acetonitrile electrolyte without added water, under argon atmosphere and hydrogen atmosphere. The spectra corresponding to the Ar-saturated solution is shown in Fig. 2a, along with an indication for the characteristic bands in the FTIR measurements. Fig. 2a shows the positive bands corresponding to C—N modes from acetonitrile in the region 2260–2340 cm⁻¹, as

well as the C—H modes from TBA⁺ at 2900–3000 cm⁻¹. The perchlorate band at 1133 cm⁻¹ is also positive in the potential range studied. No signs of residual water are registered until -1 V_{Ag/Ag⁺}. H₂-saturated solutions (Fig. 2b) show a potential-dependent negative band in the range 3400–3750 cm⁻¹, with the bending tail at 1633 cm⁻¹, indicating the depletion of water from the electrode surface with increasingly negative potential. All the other bands have a diminished intensity in presence of molecular hydrogen. These observations are consistent with the voltammeteries in Fig. 1a and b, where it was observed that the presence of H₂ brings water into the electrolyte. Fig. 2 suggests that trace amounts of water accumulate at the gold-electrolyte interface, with water depleting from the interface with more negative potential.

Addition of 50 mM of water to the electrolyte gives the spectra shown in Fig. 3a and b. In the transmission spectra we observe a small negative band around 2250 cm⁻¹ from the CN stretching modes, indicating the interaction of the electrolyte with the acetonitrile. We also observe a positive band in the range 3000–3500 cm⁻¹

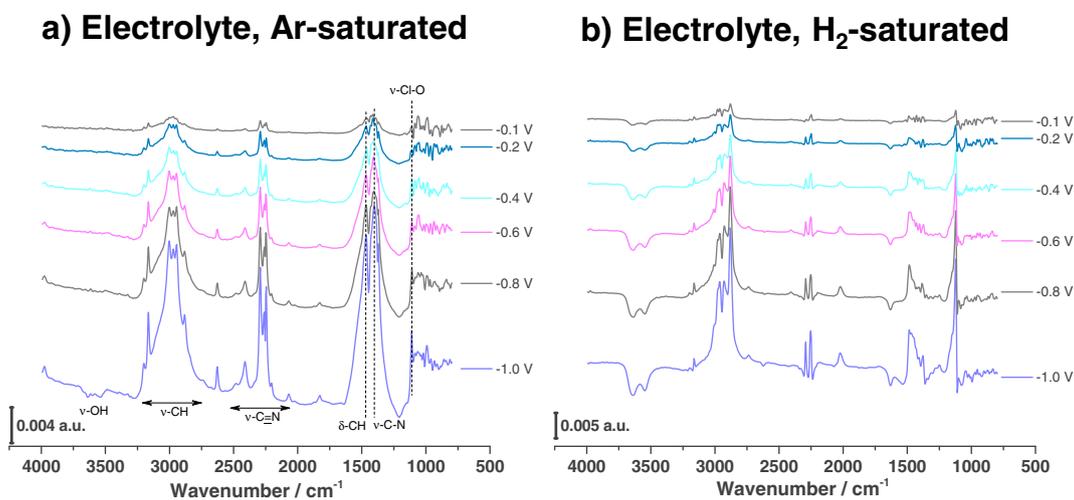


Fig. 2. Potential-dependent absorbance spectra for a polycrystalline gold electrode in acetonitrile, containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Reference spectrum recorded at 0 V_{Ag/Ag+}.

from the water stretching mode and a displaced tail from the OH deformation at 1500 cm⁻¹. The perchlorate band can be found around 1100 cm⁻¹, next to the C—H modes from the TBAP (1250 cm⁻¹). No significant differences were observed between the transmission spectra from the solution saturated with argon and the one saturated with hydrogen. From the Ar-saturated solution we recorded the potential-dependent spectra shown in Fig. 3a. Most water and electrolyte bands are negative, suggesting migration away from the electrode surface. However, the spectra show two small positive bands at 1221 and 1713 cm⁻¹. The first one is presumably related to a C—N mode of the TBA⁺ cation. The second one is characteristic

of a C—O stretching mode, the nature of which remains unclear since the acetonitrile is not expected to decompose at these applied potentials. The spectra for the H₂-saturated solution (Fig. 3b) shows all the bands from water and electrolyte pointing downwards, suggesting the movement of species away from the electrode surface.

The results presented in Figs. 2 and 3 suggest that the electrolyte TBAP interacts more strongly with the electrode when water is not present. The potential-dependent behavior of the electrolyte ions in Figs. 2 and 3 is difficult to interpret, but one must bear in mind that these measurements were performed in a thin-layer configuration,

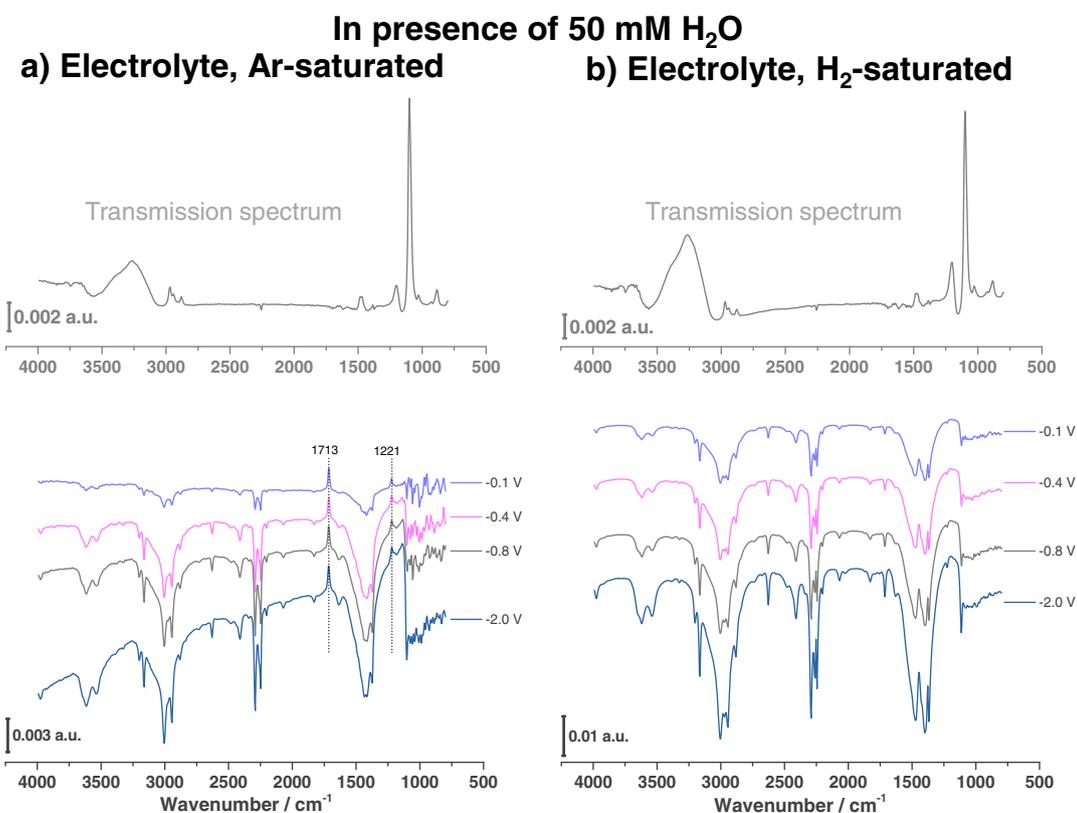


Fig. 3. Potential-dependent absorbance spectra for a polycrystalline gold electrode in acetonitrile, containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte and in presence of 50 mM of added water. Reference spectrum recorded at 0 V_{Ag/Ag+}.

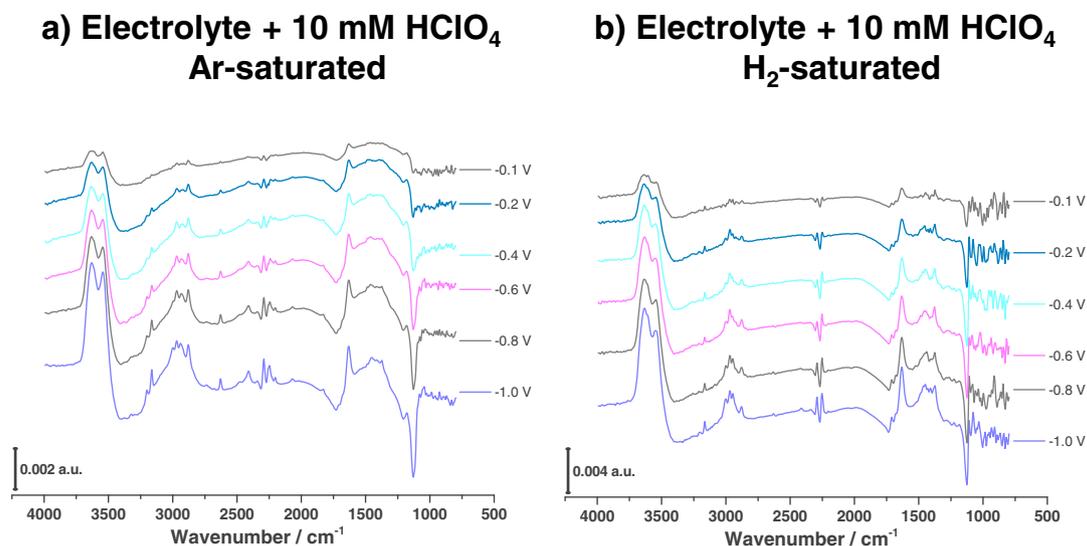


Fig. 4. Potential-dependent absorbance spectra for the hydrogen evolution on a polycrystalline gold electrode in acetonitrile, containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte + 10 mM of HClO_4 . Reference spectrum recorded at $0 \text{ V}_{\text{Ag}/\text{Ag}^+}$.

which was sometimes difficult to stabilize. Since no current is flowing, significant movement of ions is not expected, other than those adsorbing or desorbing, or moving in and out of the double layer. When a small amount of water is present or added to the electrolyte, and no apparent hydrogen evolution is proceeding, water leaves the electrode surface when a cathodic potential is applied, and this behavior is independent of the saturation gas.

The spectra presented in Figs. 2 and 3 showed the conditions of the interface in the absence of proton reduction. Now we evaluate the hydrogen evolution in the acetonitrile electrolyte in presence of a proton donor in the absence and presence of added water, under argon or hydrogen atmosphere. The results are shown in Fig. 4a and b. In Fig. 4a the accumulation of water at the electrode surface is evidenced by the double band near 3500 cm^{-1} and the water bending mode at

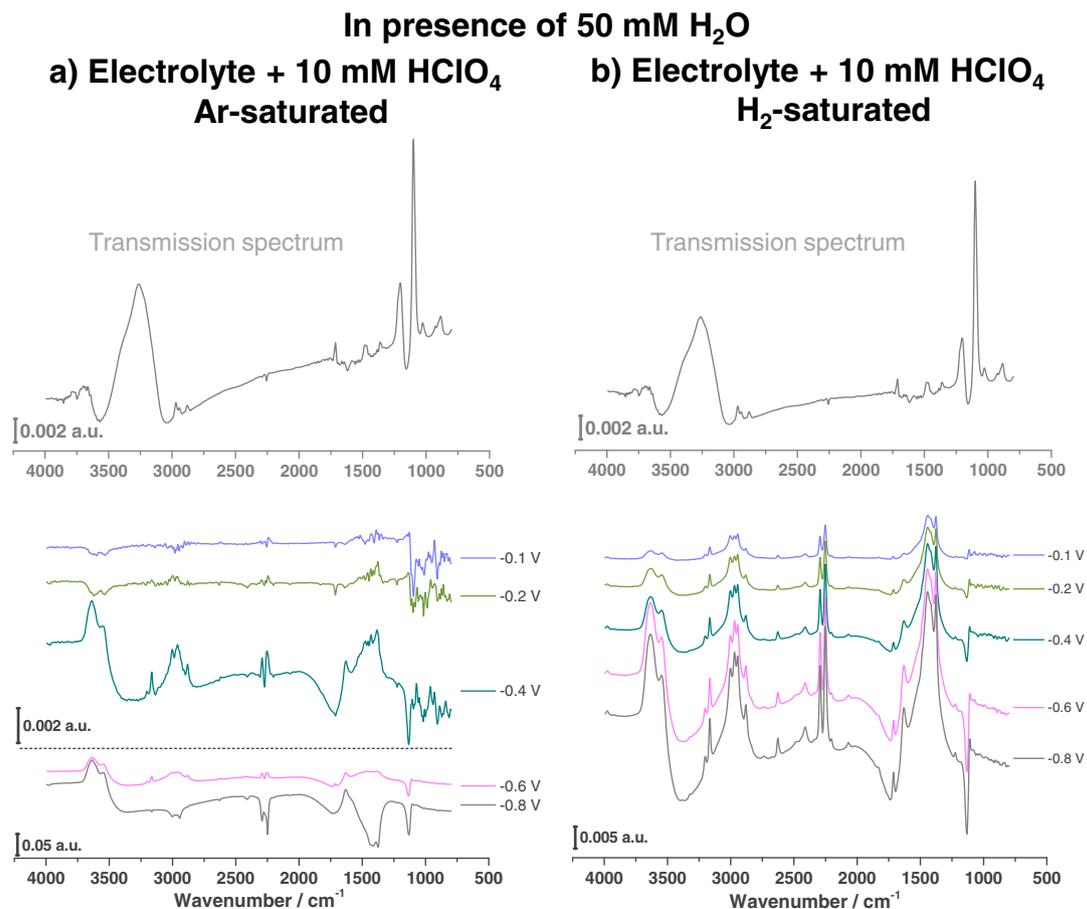


Fig. 5. Potential-dependent absorbance spectra for the hydrogen evolution on a polycrystalline gold electrode in acetonitrile, containing 50 mM of water and 0.1 M tetrabutylammonium perchlorate as supporting electrolyte + 10 mM of HClO_4 as proton donor. Reference spectrum recorded at $0 \text{ V}_{\text{Ag}/\text{Ag}^+}$.

1633 cm^{-1} . We also observe the movement of the TBA^+ and the acetonitrile towards the electrode surface, described by the positive bands from the cation C—H at 2750 to 3250 cm^{-1} and the C—N stretching modes at 2450 cm^{-1} , respectively. On the other hand, the sharp perchlorate stretching mode at 1130 cm^{-1} depletes with more negative potentials. Saturation with molecular hydrogen (Fig. 4b) leads to similar observations as in Fig. 4a, without significant changes from what is observed in the Ar-saturated solution. These observations suggest that water accumulates at the electrode surface in presence of protons, and that perchlorate anions deplete from the surface, in agreement with Faradaic current flow. This interpretation of the accumulation of water being due to the preferential solvation of protons by water is partially inspired by our previous observation with platinum electrodes [9], namely that hydrogen oxidation in acetonitrile leads to the disappearance of water from the interface, which we ascribed to the migration of protons away from the electrode surface.

In presence of added water and protons (Fig. 5), the spectra from the Ar-saturated solution initially show a depletion of water from the interface until an inversion in the band orientation is observed at $-0.4 \text{ V}_{\text{Ag}/\text{Ag}^+}$ at the onset of HER. At this potential, the water bands turn positive, indicating accumulation of water at the electrode surface. Acetonitrile and TBA^+ bands are initially positive and then invert their orientation at $-0.8 \text{ V}_{\text{Ag}/\text{Ag}^+}$, indicating the migration of electrolyte-related species from the surface as hydrogen is produced, while water is present in the double layer. Under hydrogen-saturated conditions, Fig. 5b shows all electrolyte-related bands and water migrating towards the electrode, except for the perchlorate, which leaves the surface.

Finally, we compare the HER on gold and platinum electrodes in acetonitrile solutions containing supporting electrolyte and 10 mM of HClO_4 . Fig. 6 shows the Tafel plots obtained at a scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$. We subtracted the non-Faradaic contributions from the voltammograms in order to obtain polarization curves. The measurements in Fig. 6 show Tafel slope values of $132 \text{ mV} \cdot \text{dec}^{-1}$ for a gold electrode and $137 \text{ mV} \cdot \text{dec}^{-1}$ for a platinum electrode. The Tafel slopes indicate that the hydrogen evolution on gold and platinum in acetonitrile proceed through the same rate-determining step, namely that the first electron transfer step is rate-determining for the hydrogen evolution in acetonitrile solutions on both metals. Interestingly, this mechanism resembles the mechanism for HER in alkaline aqueous solution [18] and may suggest an important role of solvent reorganization in the hydrogen adsorption step.

4. Conclusion

In this paper, we have illustrated the importance of small amounts of water in the proper description and understanding of the hydrogen

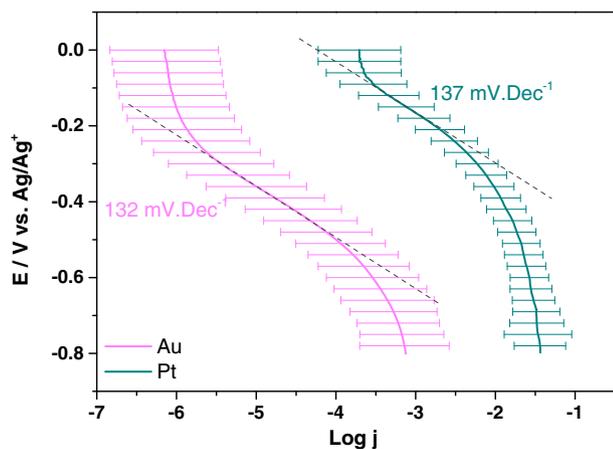


Fig. 6. Tafel plots measured for gold and platinum microelectrodes in acetonitrile in presence of 0.1 M TBA^+ as supporting electrolyte and 10 mM HClO_4 as proton donor. Argon atmosphere.

evolution reaction at a gold electrode in acetonitrile. The FTIR studies reveal that trace amounts of water accumulate at the gold-acetonitrile interface. Karl Fischer analysis of the electrolyte solutions shows that the largest source water is the electrolyte salt, not the acetonitrile itself, but also the bubbling of hydrogen brings water into the solution. In absence of protons and Faradaic current, the water migrates away from the surface into the bulk with more negative potentials. On the other hand, in presence of added proton source, under HER conditions, water accumulates at the electrode surface with more negative potential, indicating that protons attract water to the surface during their migration as a consequence of preferential solvation. This conclusion is underlined by experiments with purposefully added water. A similar observation has been made previously for hydrogen evolution on platinum electrodes in acetonitrile [9]. Regarding the migration of anions and cations in the acetonitrile solutions, under conditions of Faradaic current, they behave in accordance with the applied potential, i.e. TBA^+ cations migrate towards the surface and perchlorate anions move away at applied cathodic potentials. In the absence of Faradaic current, the behavior of the motion of ions is not fully understood but it should be noted that the thin-layer configuration under which the FTIR measurements were performed may not be stable enough to draw clear conclusions.

From the Tafel plot analysis we conclude that the hydrogen evolution on gold and platinum proceeds via the same mechanism in the sense that the rate-determining step for the hydrogen evolution in (water-containing) acetonitrile is the first electron transfer, leading to the adsorption of atomic hydrogen.

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