The role of water in hydrogen electrocatalysis

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2. Hydrogen oxidation and hydrogen evolution on a platinum electrode in acetonitrile

ABSTRACT

This work discusses the kinetics of the hydrogen oxidation and evolution on a polycrystalline platinum electrode in acetonitrile, in presence of two different electrolytes. Our findings point out the sensitivity of the kinetics of these reactions to the presence of small amounts of water. In situ Infrared Spectroscopy (FTIR) reveals the ion migration owing to the preferential solvation of protons in residual water, whereas the Surface Enhanced Raman Spectroscopy (SERS) confirms that the water leaves the interface under hydrogen oxidation conditions. These observations imply that the kinetic sensitivity of this electrocatalytic reaction towards the preferential solvation processes presents a serious constraint in the establishment of a reference electrode for non-aqueous solvents based on the HOR/HER on platinum, and on the comparison of its catalysis in various non-aqueous solvents.

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2.1. Introduction

The hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER) are key reactions in electrochemistry,[1] as well as in the development of technologies towards clean energy and fuel cells. The majority of the electrochemical studies of HOR/HER have pertained to aqueous electrolytes. With the search for new, cheap, and efficient catalysts for HER, studies of molecular catalysts often employ non-aqueous solvents, such as acetonitrile, for activity testing.[2] Having a standard activity test in the same solvent then becomes desirable, including detailed insight into the molecular mechanisms involved in this standard system. Platinum would be the most suitable electrode material for such a benchmark activity test, as it is for tests in aqueous electrolytes. Although several studies on the HER and HOR in acetonitrile[3] have been carried out, comparatively little has been settled about the mechanism involved, such as the role of cations, anions and residual water, leading to an incomplete understanding of the process and its catalysis.

Acetonitrile is an aprotic solvent that has proved to be convenient for use in electrochemistry,[4] primarily related to its miscibility with water, combined with a relatively high dielectric constant (37.5), giving excellent solvation properties for a variety of electrolytes. However, ion pairs can form in acetonitrile[5] and, under certain conditions, they can also adsorb strongly or even dissociate on the electrode surface,[6] under the influence of an electrode potential. These features make acetonitrile especially sensitive to the use of different supporting electrolytes for hydrogen oxidation and hydrogen evolution, leading to voltammetric responses that have proved difficult to interpret.

Early work by Chambers[1f] and Sawyer[7] demonstrated the high sensitivity and even irreproducibility to electrolyte parameters of HER and HOR activity on a platinum electrode in acetonitrile. More recent findings reported by Suárez-Herrera *et al.*[3c] highlighted the role of the nature of cations and the presence of water on

the HOR activity on single-crystal platinum electrodes in acetonitrile. Their *in situ* infrared data revealed that chemisorption of hydrogen, acetonitrile and cyanide takes place only when water is present in the interface. Interestingly, they propose that hydrogen oxidation on platinum in acetonitrile is mediated by hydroxyl groups present on the electrode surface, as formed by the oxidation of residual water. According to their results, the proton released in this process is stabilized by forming an ion pair with the electrolyte anion. This proposition is in agreement with the earlier observation that oxidation of Pt activates the surface for the HOR in acetonitrile.[7] Those conclusions lead to the intriguing apparent paradox that in acetonitrile, HOR takes place on an oxygen-covered Pt surface, whilst in aqueous electrolyte, HOR takes place on hydrogen-covered Pt surface.[8] It also raises the question whether Pt is really a suitable activity standard for HOR/HER in acetonitrile.

In this work, we present a combined electrochemical and *in situ* spectroscopic study of the HOR/HER reaction on platinum in acetonitrile. We aim to understand (i) how the interaction of the acetonitrile with the electrolyte ions and with platinum[6, 9] affects the catalytic activity, and (ii) how a small amount of water interferes with the catalytic activity in the presence of two different cations, i.e. tetrabutylammonium TBA^+ and lithium Li^+, expecting the latter to have a stronger specific interaction with water. Our results show that the HOR/HER on Pt is a reversible process in acetonitrile, but also that there is a crucial role of water and cations. According to our findings, the role of water seems to be primarily in the preferential solvation of protons and other small cations, rather than in the activation of the platinum surface.

2.2. Experimental Section

Solutions were prepared using acetonitrile as received (Anhydrous 99.8%, from Sigma-Aldrich). As proton source, we used perchloric acid (70% *Suprapur*®

Merck). $LiClO_4$ and tetrabutylammonium perchlorate for electrochemical analysis (99.0% from Sigma-Aldrich) were used as supporting electrolytes. Ferrocenium hexafluorophosphate (97%, from Sigma-Aldrich) and ferrocene (99%, from Alfa Aesar) were used in equimolar concentration to calibrate the equilibrium potential of the $Ag/AgClO_4$ reference electrode used in this work. All the solutions were purged with argon (purity grade 6.0), whereas for the experiments performed under hydrogen atmosphere we used a constant hydrogen flux (purity grade 5.6). No further attempts were made to dry the electrolyte solutions.

Prior to experiments, the glassware was rinsed with water (Milipore® MiliQ; resistivity >18.2 MΩ.cm), then rinsed with acetone (Sigma-Aldrich), and placed in the oven over night, at 120 ℃.

For the electrochemical measurements we used an Ivium potentiostat/galvanostat (IviumStat) connected to a one-compartment, three-electrode cell. The working electrode (WE) was a platinum wire with a diameter of 120 μm and a real surface area of $(5{,}9 \pm 0{,}1) \times 10^{-4}$ cm^2, measured from the hydrogen adsorption/desorption in aqueous solution,[10] assembled to a glass stem and flame annealed before each measurement. The counter electrode (CE) consisted of a platinum spiral, while the reference electrode (RE) was a home-made $Ag/AgClO_4$ in acetonitrile. The RE consisted on a silver wire immersed in a glass tube, filled with a 1 mM $Ag/AgClO_4$ solution in acetonitrile. The tube has a glass-junction, allowing the free transport of ions from the luggin into the electrolyte. A 10 μF capacitor was connected between the RE and a platinum wire immersed in the solution, as a noise filter. In order to calibrate the zero in the $Ag/AgClO_4$ RE scale respect the SHE scale, we prepared a ferrocene/ferrocenium solution in an equimolar concentration (10 mM), as the accepted internal standard for electrochemical measurements in non-aqueous solutions, and measured its cyclic voltammetry against the $Ag/AgClO_4$ RE. The equilibrium potential of the redox couple Fc^0/Fc^+ was calculated as the half wave potential in the cyclic voltammetry and the measured value is 0.038 V.

Surface Enhanced Raman Spectroscopy (SERS) measurements were performed with a confocal Raman microscope (LabRam HR, Horiba Yobin Yvon), equipped with a He/Ne laser (633 nm) and a 50X objective. The electrochemical measurements were controlled with a METROHM μAUTOLABIII potentiostat/galvanostat, using an electrochemical cell with one compartment and three electrodes: a platinum wire as CE, $Ag/AgClO_4$ in acetonitrile as RE, whereas the working electrode consisted of 2 ML of platinum deposited galvanostatically from an aqueous 100 mM H_2PtCl_6 solution on a roughened gold surface.[11] The gold surface was previously polished with alumina (different mesh; e.g. 1 μm, 0.3 μm and 0.05 μm), rinsed with ultrapure water and sonicated during ten minutes to remove any alumina residues remaining. The roughening procedure has been reported in the literature[12] and consists on immersing the electrode in a 100 mM KCl solution and perform 25 oxidation-reduction cycles, between -0.30 V and 1.20 V vs. SCE, by holding the cathodic potential for 30 s and the anodic potential for 1.3 s.

The Fourier Transform Infra-Red Spectroscopy (FTIRS) measurements were carried out in a three electrode cell coupled to a CaF_2 prism slanted at 60 degrees, and connected to a Bruker Vertex80V IR spectrophotometer. The WE was a platinum disc settled in a thin layer configuration, the CE was a platinum wire and the RE was $Ag/AgClO_4$ in acetonitrile. Hundred interferograms were averaged for each spectrum, with a resolution of 8 cm^{-1}, as well as for the measurement of the transmission spectra, whose reference spectrum was taken from pure acetonitrile. The spectra in this work are reported as difference spectra with respect to a background spectrum, and normalized against such reference, $(T-T_0)/T_0$. Hence, bands pointing upwards correspond to the depletion of species at the electrode surface and will be called positive bands, while bands pointing downwards indicate the adsorption of species and will be assigned as negative bands.

2.3. Results

2.3.1. Reference scale: from Ag^0/Ag^+ to SHE.

In this work we employ a practical reference scale suitable for the H^+/H_2 couple in acetonitrile. Fourmond et al.[2d] have recently reconsidered the standard potential of the hydrogen couple in acetonitrile, E_{SHE}^{MeCN}, measured using a molecular catalyst, and reporting an estimated value of -0.070 V vs Fc^0/Fc^+, which corresponds to -0.033 V vs. our $Ag/AgClO_4$ electrode in acetonitrile. However, standard conditions are generally not achievable due to the low dissociation constant of acids in organic solvents, including perchloric acid in acetonitrile (pk_a=1.57)[13]

Therefore,

$$E_{H^+/H_2}^{eq,MeCN} = E_{H^+/H_2}^{0,MeCN} + \frac{RT}{2F} ln \frac{[H^+]^2}{pH_2} \quad \text{(Eq. 1)}$$

$$E_{\frac{H^+}{H_2}}^{eq,MeCN} = E_{SHE}^{MeCN} + \frac{RT}{2F} ln \frac{(\alpha c)^2}{pH_2} \quad \text{(Eq. 2)}$$

where α is the degree of dissociation, and *c* is the nominal concentration of the HA acid.

We note that there is still considerable uncertainty in the "real" value of E_{SHE}^{MeCN}. The estimated value quoted by Fourmond *et al.* deviates from previous values, and is also ca. 0.1 - 0.2 V different from theoretical estimates by Fawcett[14]. In the voltammetric curves shown below, V_{SHE} is understood as the electrode potential referred to E_{SHE}^{MeCN}.

2.3.2. Voltammetry for HOR/HER in acetonitrile

Figures 1 and 2 show the cyclic voltammograms for polycrystalline platinum in acetonitrile, using tetrabutylammonium perchlorate (TBAP; black solid line) or

$LiClO_4$ (red dashed line) as supporting electrolytes. Fig. 1a shows the hydrogen oxidation in the base electrolyte in the absence of proton donor. Fig. 1b shows the hydrogen evolution in the presence of 10 mM $HClO_4$ in an Ar saturated electrolyte. Finally, Fig.1c combines HOR and HER in the presence of 10 mM $HClO_4$ in a H_2 saturated electrolyte. In each subfigure (a to c), we present the last cycle out of 200 scans between 1.0 and -1.0 V_{SHE}, starting the sweep at 0.1 V_{SHE} in the cathodic direction. The blank voltammetry of Pt in both electrolytes is rather featureless and is shown in the Appendix A, Figure A1. In both electrolytes, there is a pair of reduction/oxidation peaks that is observed clearly in the first scan but disappears quickly in subsequent scans. The HER/HOR currents are sensitive to the scan rate in both electrolytes (Fig.A2). Especially, the HOR current lowers with lower scan rates, whereas the system with TBAP exhibits a larger HER current in the acidic solution. In general, the HER/HOR becomes more reversible at high scan rates for both electrolytes, suggesting the presence of a slow deactivation process in the system.

Figure 1a shows the voltammetry recorded for the solution saturated with hydrogen, with the peak for the hydrogen oxidation presenting a similar current and shape for both electrolytes. In the negative-going scan, the proton reduction peak is observed, and is somewhat larger for the $LiClO_4$ electrolyte. In Figure 1b, the voltammetries for solutions containing 10 mM $HClO_4$ for each electrolyte, saturated with Ar, should have a real proton concentration of 2.1 mM as calculated from the pK_a of the acid. Obviously, the proton reduction peak in Figure 1b has a higher current compared to the same peak in Figure 1a. A small current is observed in the positive-going scan, corresponding to the oxidation of H_2 formed in the previous cathodic scan. Evaluation of the HER/HOR couple in Figure 1c shows a similarly shaped proton reduction peak in comparison with Figure 1b, (though the current is slightly larger in Figure 1c, due to proton formation in the oxidation of molecular hydrogen). However, the HOR current is considerably smaller than in the proton-free electrolyte solution depicted in Figure 1a.

Figure 2 shows the cyclic voltammetries for polycrystalline platinum in acetonitrile, using TBAP (black solid line) or $LiClO_4$ (red dashed line) as supporting electrolytes, in presence of 50 mM H_2O. Figure 2a compares the blank voltammetries for both electrolytes and shows that the background current for the solution with $LiClO_4$ is one order of magnitude larger compared with the solution containing TBAP. For the $LiClO_4$ electrolyte, the onset potential for water reduction is ca. -0.750 V_{SHE} (see Figure A1a). In the anodic sweep, there is a corresponding oxidation peak, which, however, cannot be due to hydrogen oxidation, since that is expected to occur only at much more positive potentials (see Figure 1a). For the TBAP electrolyte, no significant water reduction current is observed in this potential window. After saturating the solutions with hydrogen, Figure 2b depicts the HOR process in the presence of water. The voltammetry obtained for TBAP electrolyte is very similar to the voltammetry presented in Figure 1a for the HOR in absence of added water, although the hydrogen oxidation current is slightly smaller than in Figure 1a, while the reduction current peak is comparatively larger. A much more significant influence of water is observed for the $LiClO_4$ electrolyte. Figure 2b shows an irreversible behavior and a much lower redox current. Addition of 10 mM $HClO_4$ to the solutions with water and saturating them with hydrogen gas, leads to the voltammetric responses shown in Figure 2c. Remarkably, the proton reduction wave is very similar for both electrolytes, and not significantly different from the system in Figure 1c, but the hydrogen oxidation is significantly inhibited by the combination of Li^+ and water.

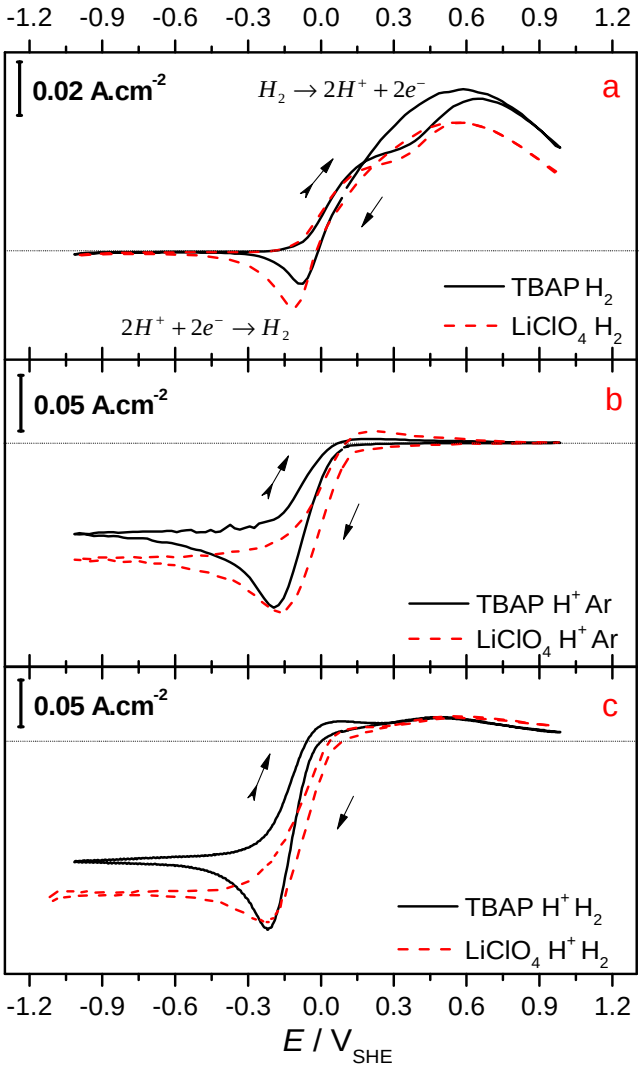

Figure 1. Cyclic voltammetries for a polycrystalline platinum wire in acetonitrile, containing 100 mM $LiClO_4$ (red dashed line) or 100 mM TBAP (black solid line), as supporting electrolytes. a) Hydrogen saturated; b) After adding 10 mM $HClO_4$; argon saturated; c) After adding 10 mM $HClO_4$; hydrogen saturated. Scan rate: 500 mV/s, in order to minimize gradual solvent decomposition[15]. The horizontal dotted lines mark zero current.

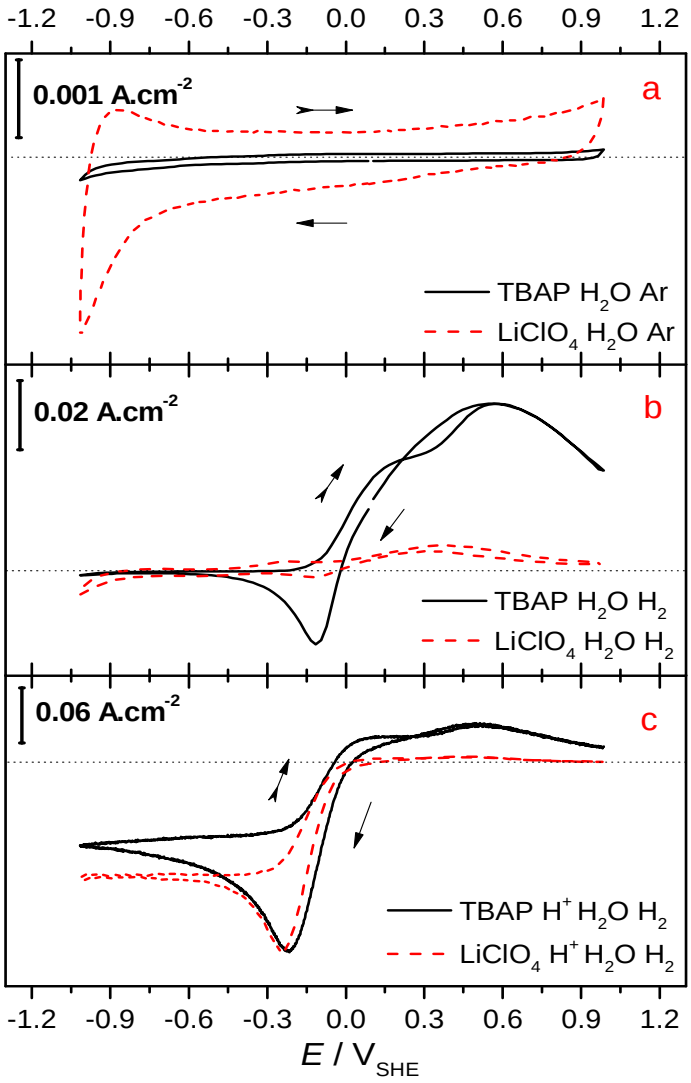

Figure 2. Cyclic voltammetries for a polycrystalline platinum wire in acetonitrile, containing 100 mM $LiClO_4$ (red dashed line) or 100 mM TBAP (black solid line), as supporting electrolytes, in presence of 50 mM H_2O. a) Argon saturated; b) Hydrogen saturated; c) Adding 10 mM $HClO_4$; hydrogen saturated. Scan rate: 500 mV/s. The horizontal dotted lines mark zero current.

2.3.3. Fourier Transform InfraRed Spectroelectrochemistry.

2.3.3.1. Transmission spectra.

In order to properly evaluate the relevant interactions between solvent and other electrolyte components, we first measured the transmission spectra for acetonitrile in the presence of $LiClO_4$ or TBAP as supporting electrolytes, in an Ar-saturated electrolyte, in an H_2-saturated electrolyte, in an Ar-saturated electrolyte containing 10 mM $HClO_4$, and finally in an H_2-saturated electrolyte containing 10 mM $HClO_4$. Results are shown in Figures 3 (for $LiClO_4$) and 4 (for TBAP). These spectra are difference spectra, i.e. the spectrum for pure acetonitrile was subtracted from the electrolyte spectra. The bands identified in the spectra will be discussed according to the relevant solution components, i.e. acetonitrile, perchlorate and water, in agreement with the bands reported in the literature[16].

Acetonitrile (AN) shows bands in the 2940-3000 cm^{-1} range, ascribed to the v-CH modes,[17] and in the 2260-2340 cm^{-1} range, corresponding to the C-N bending and stretching modes. The C-H modes are naturally more prominent in presence of TBAP, due to the butyl chains of the TBA cation. The most remarkable difference is in the 2260-2340 cm^{-1} region for the two electrolytes. The spectra for the system containing $LiClO_4$ show two clear bands pointing downwards at 2307 and 2275 cm^{-1}, and one band pointing upwards at 2256 cm^{-1} ascribed to the CN bending and the CN stretching modes. These bands are essentially undisturbed by the presence of H_2 and protons (or water) in the transmission spectra. On the other hand, for the solution with TBAP (Figure 4) we observe the bands in the 2260-2340 cm^{-1} window to point upwards in presence of argon or molecular hydrogen. These bands present a blue shift when compared to the equivalent spectra in Figure 3. In addition, the presence of $HClO_4$ (and water) changes the nature of these bands in TBAP.

The perchlorate ion is characterized by the Cl-O stretching vibration around 1100 cm^{-1}. High- and low-frequency shoulders on the main band at 1100 cm^{-1} have

been ascribed to perchlorate involved in the formation of contact ion pairs (CIP). Barthel and Deser have shown the existence of such ion pairs in (more concentrated) $LiClO_4$ solutions in AN.[16a] These CIP are due to interactions between perchlorate anions and the cations, surrounded by solvent molecules. The observation of a shoulder near 1130 cm^{-1} in the $LiClO_4$ electrolyte confirms the existence of ion pairs in this electrolyte. In TBAP, these features are much less prominent.

Finally, water bands between 3100-3750 cm^{-1} (O-H stretching region) and 1550-1900 cm^{-1} (O-H bending region) are observed. This illustrates that we must count on the presence of trace amounts of water in “dry” AN with added electrolyte, and substantial amounts of water in AN acidified with $HClO_4$. No significant differences were observed between the blank solutions saturated with argon and saturated with hydrogen.

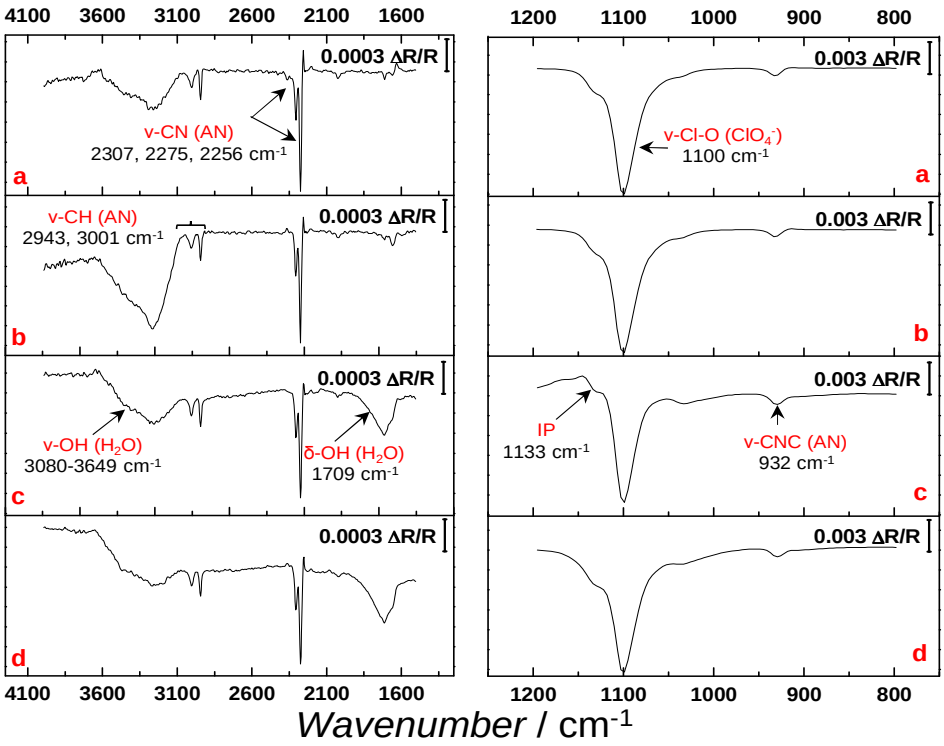

Figure 3. Transmission spectra for acetonitrile, containing 100 mM $LiClO_4$ as supporting electrolyte: a) Argon-saturated; b) Hydrogen saturated; c) After adding 10 mM $HClO_4$, Ar-saturated and d) After adding 10 mM $HClO_4$, H_2-saturated. The spectrum for pure acetonitrile was subtracted and the spectra in the figures correspond to difference spectra. (IP stands for ion pairs).

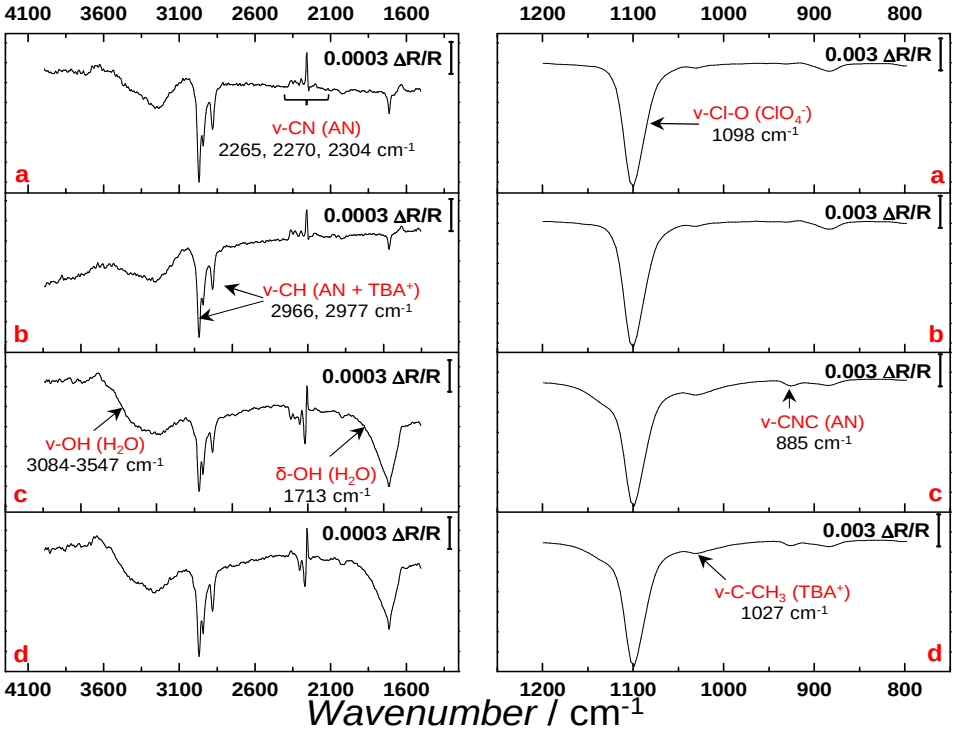

Figure 4. Transmission spectra for acetonitrile, containing 100 mM TBAP as supporting electrolyte: a) Argon-saturated; b) Hydrogen saturated; c) After adding 10 mM $HClO_4$, Ar-saturated and d) After adding 10 mM $HClO_4$, H_2-saturated. The spectrum for pure acetonitrile was subtracted and the spectra in the figures correspond to difference spectra.

2.3.3.2. Substractively Normalized Interfacial Fourier Transform Infrared Spectroscopy (SNIFTIRS).

Figures 5 and 6 show the potential-dependent SNIFTIR spectra for platinum in acetonitrile, containing 100 mM TBAP or $LiClO_4$ respectively, under different conditions. The spectra were taken from negative towards positive potentials (bottom to top in each subfigure), and plotted as difference spectra with the reference spectrum taken at -0.314 V_{SHE}. By convention, the bands pointing upwards are ascribed as positive bands, whereas the bands pointing downwards correspond to negative bands. Some of the characteristic bands from the acetonitrile electrolyte described in the previous section are present in the spectra shown in Figures 5 and 6.

Figure 5a (top panels) shows the spectra for the TBAP-acetonitrile electrolyte in the absence of H_2 or proton donor. As depicted in the figure, the C-H and C-N vibrations are potential dependent, due to a change in orientation of the near-surface AN as a result of the applied potential.[9] Under conditions of hydrogen oxidation at the platinum electrode (Fig.5b, middle panels), we observe two important changes: the appearance of a positive band in the O-H stretching region (3300 – 3750 cm^{-1}) and O-H bending region (tail observed at 1633 cm^{-1}), indicating that water is depleting from the electrode surface; and the development of a negative band in the Cl-O stretching region around 1130 cm^{-1}, indicating that perchlorate anions are attracted or migrating to the electrode surface. In the presence of $HClO_4$ the same bands are observed. The most likely interpretation of these results is that the protons generated by H_2 oxidation are preferentially solvated by water. Under oxidation conditions, these water-solvated protons move away from the surface (hence the observed depletion by water) and the perchlorate ions migrate towards the surface. No significant difference was found between the features for the system with and without acid, in presence of H_2, other than that the water-related band appear at lower potentials in the presence of acid.

Figure 6 shows the FTIR spectra for platinum in acetonitrile, containing 100 mM $LiClO_4$, under the same conditions as in Figure 5. Qualitatively, the spectra are similar to Figure 5 but some significant differences can nevertheless be observed. In the system saturated with argon (Fig. 6a, top panels) we observe the CN stretching modes for acetonitrile. In presence of hydrogen (Fig. 6b, middle panels) we observe the occurrence of a third shoulder around 3469 cm^{-1} in the O-H stretching region (3300 – 3750 cm^{-1}), which may be attributed to the interaction of water with the Li^+, since it is not observed for the systems with TBAP (compare Figures 5 and 6). These observations are complementary to the observations in Figure 5, since the lithium cation shows preferential solvation in presence of water[18] and implies that the water is leaving the surface by solvating and migrating with Li^+ and the H^+ formed during the hydrogen oxidation

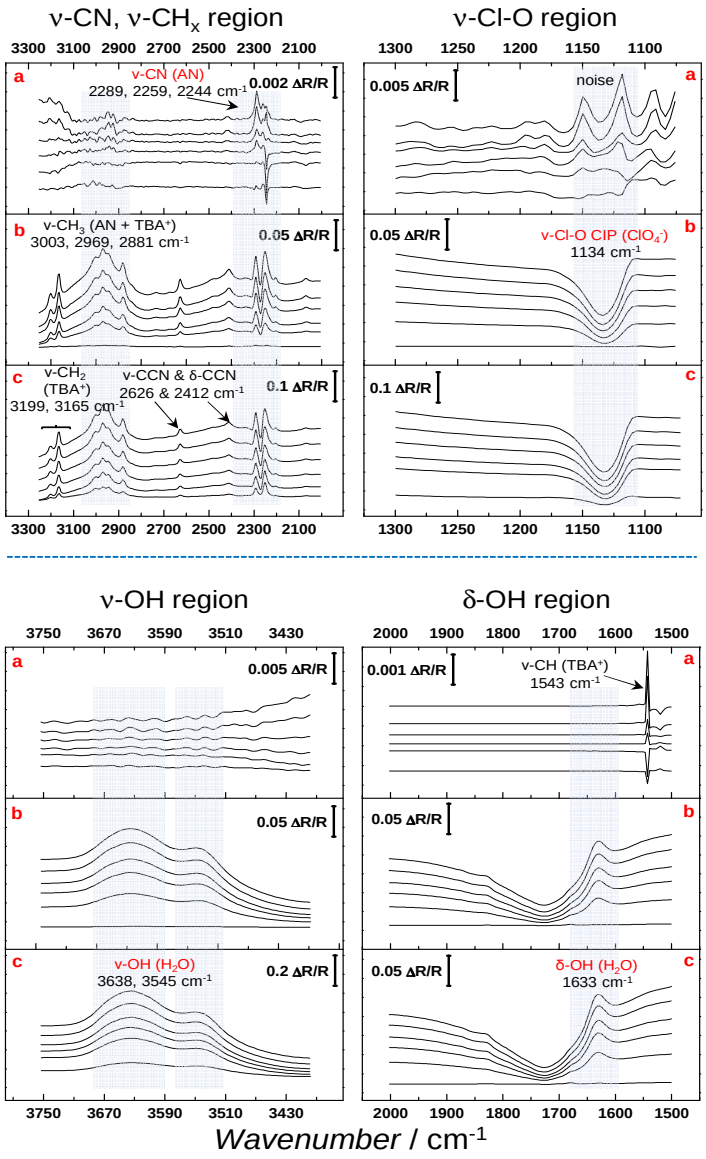

Figure 5. Potential-dependent SNIFTIR spectra for a polycrystalline platinum electrode in acetonitrile, containing 100 mM TBAP as supporting electrolyte: a) Argon atmosphere; b) Hydrogen atmosphere; c) After adding 10 mM $HClO_4$ under hydrogen atmosphere. Reference spectrum: -0.500 V_{Ag^0/Ag^+} (corresponding to -0.314 V_{SHE}).

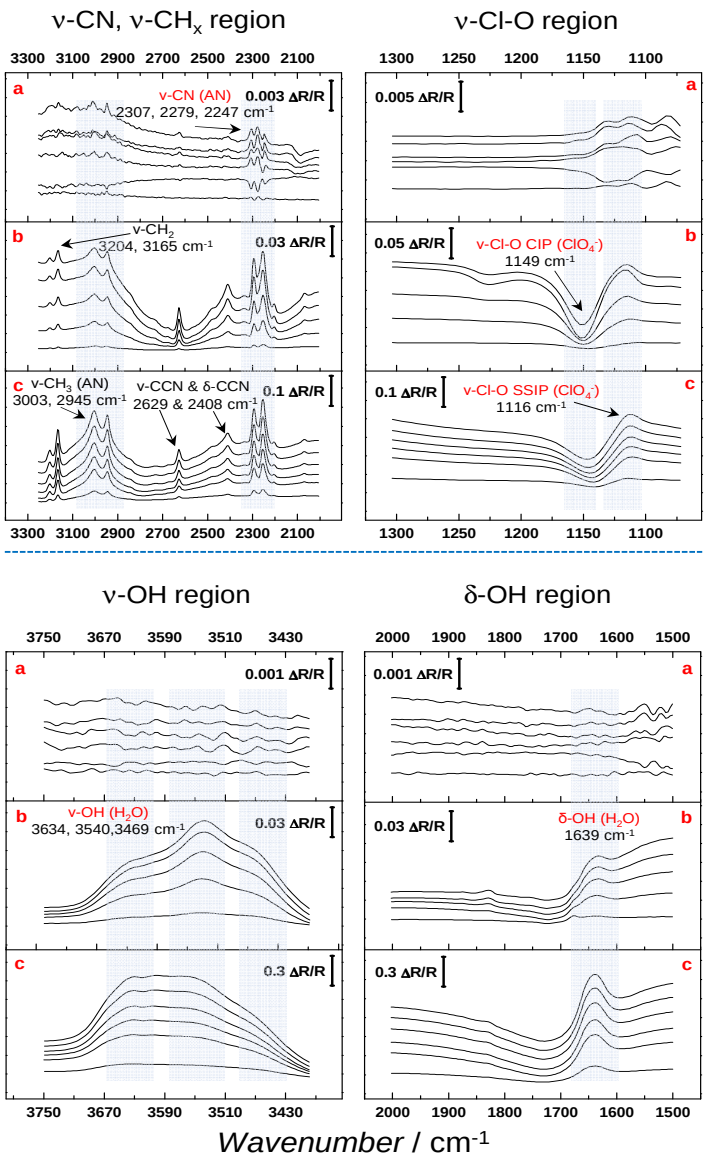

Figure 6. Potential-dependent SNIFTIR spectra for a polycrystalline platinum electrode in acetonitrile, containing 100 mM $LiClO_4$ as supporting electrolyte: a) Argon atmosphere; b) Hydrogen atmosphere; c) After adding 10 mM $HClO_4$ under hydrogen atmosphere. Reference spectrum: -0.500 V_{Ag^0/Ag^+} (corresponding to -0.314 V_{SHE}).

2.3.4. Surface Enhanced Raman Spectroscopy (SERS).

The potential-dependent SER spectra for platinum in acetonitrile containing 100 mM electrolyte are shown in Figures 7 and 8. The spectra from 100 to 2250 cm^{-1} are shown in the Figures A3 and A4. The Figures presented below correspond to the region 2000 to 2200 cm^{-1}. The bands depicted here appear around 2070 cm^{-1} and 2140-2160 cm^{-1} and have been reported[6] as the v-CN vibrations from isocyanide adsorbed on the surface of the electrode, i.e. with N binding to the Pt. In agreement with the report by Tian and coworkers,[6] this suggests that acetonitrile decomposes on the platinum surface, especially at more negative potential (the potential window in their measurements was 0.7 V more negative than ours). They also observed that the presence of water inhibits the acetonitrile decomposition. Interestingly, under conditions of water removal from the surface (H_2 oxidation) at positive potential, the (iso)cyanide bands at 2050-2150 cm^{-1} appear. The bands are much weaker (and even absent in TBAP electrolyte in our potential window) when no hydrogen oxidation/proton generation takes place. This could be interpreted as a “protective layer” of water on the Pt surface under unreactive conditions, which is removed by the generation of protons that are preferentially solvated by water.

The band positions are potential dependent, as observed by Tian *et al*.,[6] and also cation dependent. The (iso-)cyanide bands are not present in the system containing TBA^+ saturated with argon (see Figure 7, top panel), while in presence of Li^+ and argon-saturated, only one of the bands attributed to the isocyanide stretching can be observed, but with a low intensity (see Figure 8, top panel). As mentioned, we ascribe the enhancement of these bands in both systems saturated with hydrogen to the removal of water from the interface by hydrogen oxidation.

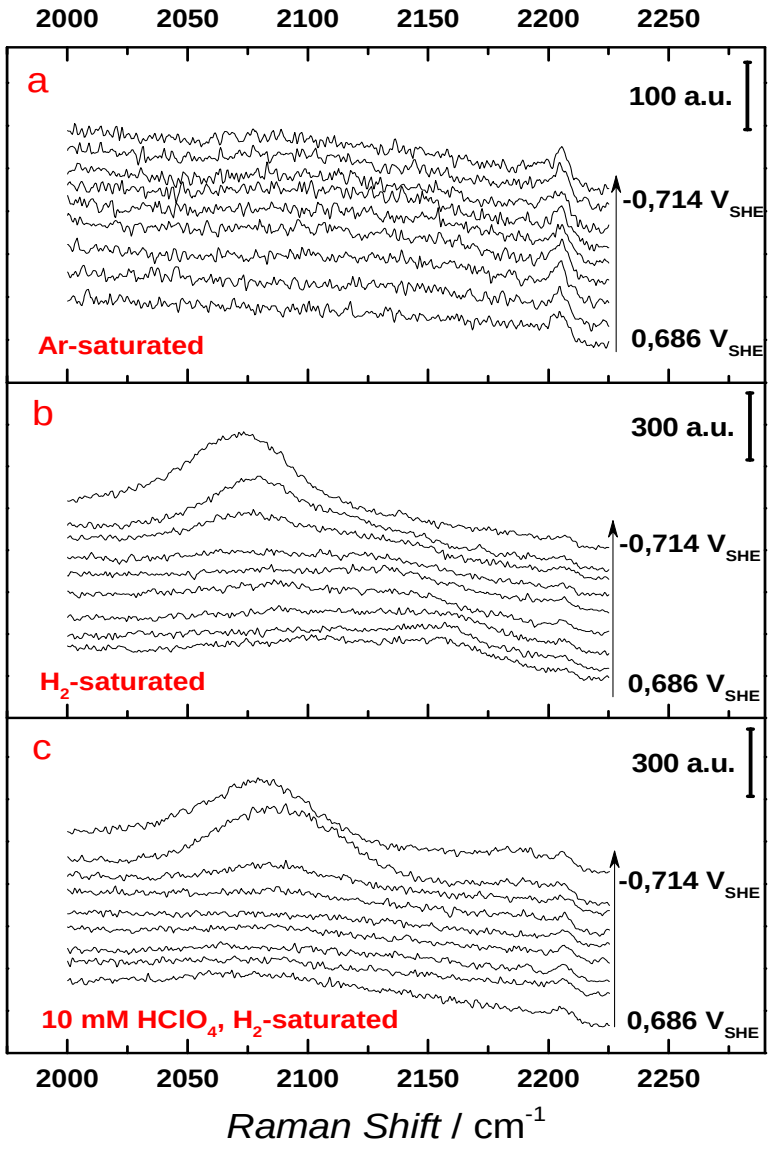

Figure 7. Potential-dependent SER spectra for acetonitrile, containing 100 mM TBAP as supporting electrolyte: a) Argon atmosphere; b) Hydrogen atmosphere; c) After adding 10 mM $HClO_4$; hydrogen atmosphere.

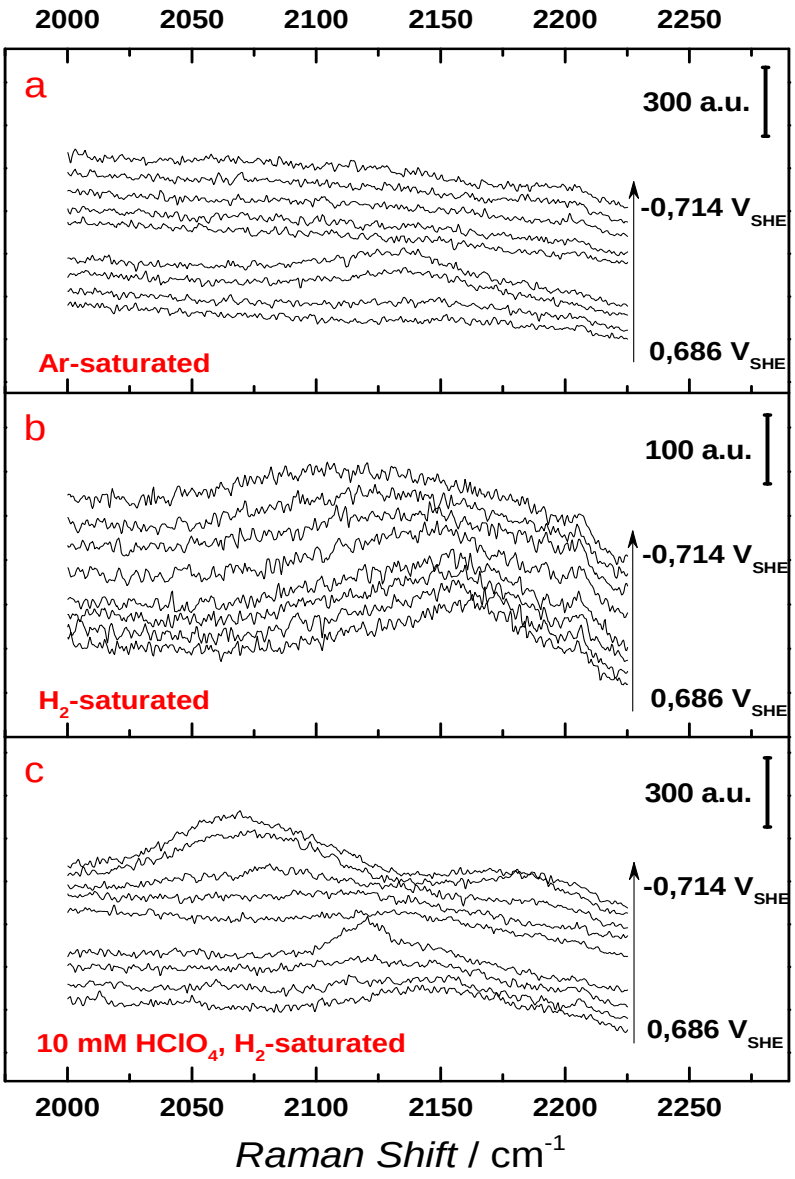

Figure 8. Potential-dependent SER spectra for acetonitrile, containing 100 mM $LiClO_4$ as supporting electrolyte: a) Argon atmosphere; b) Hydrogen atmosphere; c) After adding 10 mM $HClO_4$; hydrogen atmosphere.

Finally, Figure 9 shows the SER spectra of the region 400-850 cm^{-1} for acetonitrile in presence of TBAP and 50 mM of water. The spectra from 100 to 3500 cm^{-1} are shown as Figure A4 in the Appendix A. In the top panel we observe the formation of a broad band at high potentials of ca. 0.8-0.9 V_{SHE} centered ca. 570 cm^{-1}, reported[19] as a mixture of Pt-O and α-PtO_2. Again, this suggests that water is present at the Pt-acetonitrile interface, and it becomes oxidized at sufficiently positive potential. However, the platinum oxide band is not observed for the hydrogen-saturated solution, as shown in the bottom panel of Figure 9. This is consistent with our conclusion that water is removed from the interface under conditions of hydrogen oxidation. We note that these experiments were performed only in a solution containing TBAP as supporting electrolyte, since the $LiClO_4$ forms visible aggregates on the electrode surface in presence of 50 mM of water, presumably due to the formation of LiOH.[20]

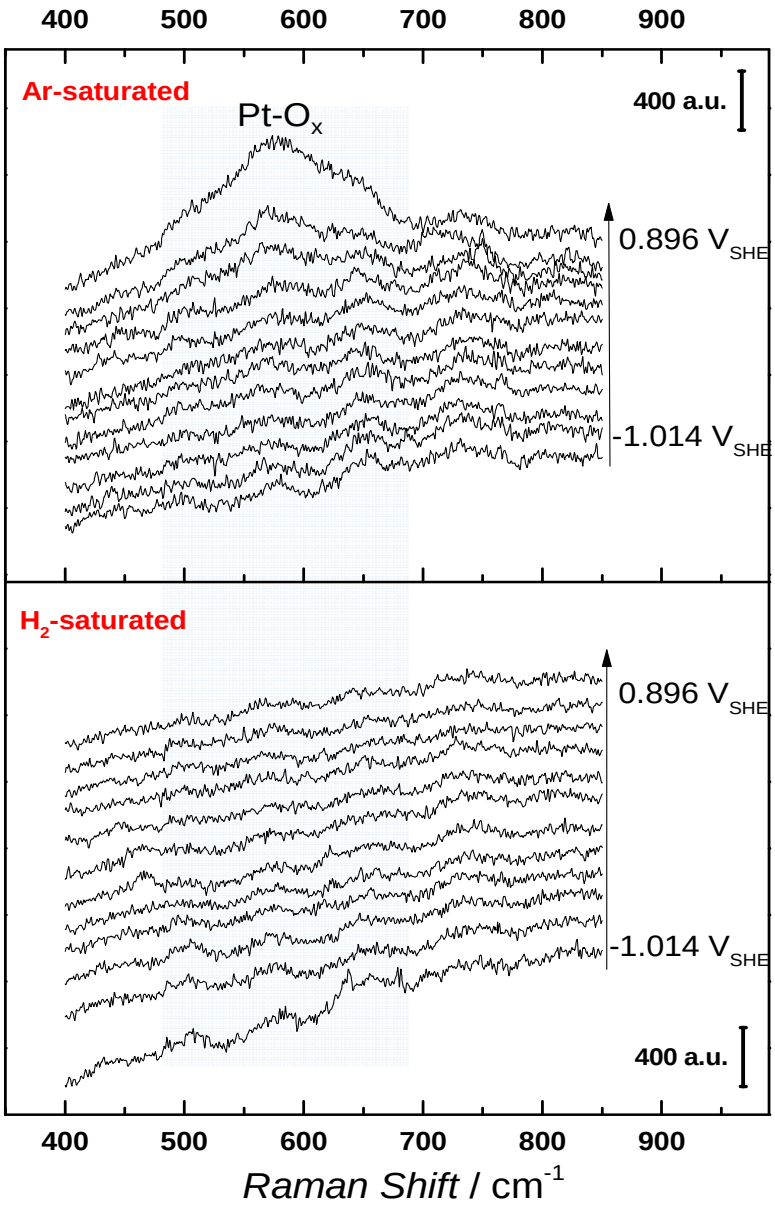

Figure 9. Potential-dependent SER spectra for acetonitrile, containing 100 mM TBAP as supporting electrolyte, in presence of 50 mM of water.

2.4. Discussion

Our aim in this paper was to categorize and ultimately understand the differences and similarities in kinetics of the HOR/HER in acetonitrile in the presence of two supporting electrolytes, their main difference being the nature of the cation, i.e. the tetrabutylammonium cation, as a hydrophobic/lipophilic cation, vs. Li^+ as a metallic, hydrophilic cation. Since our solutions contained trace amounts of water from different sources (primarily from the electrolyte and the acid), we purposefully added a controlled amount of water to evaluate its effect more clearly. Our results point out the high sensitivity of the HOR/HER kinetics in acetonitrile towards the presence of even small amounts of water.

The voltammetry of HOR and HER in acetonitrile (Figure 1) shows that their kinetics is relatively insensitive to the nature of the electrolyte cation. The reaction is reversible and the observed equilibrium potential corresponds well with the expected reversible potential. From the voltammetry, the addition of water (Figure 2) appears to have a limited influence, with the exception of a significant lowering of the HOR current in the Li^+-containing electrolyte. It has been reported that Li^+ can associate with hydroxyl groups from water to form LiOH aggregates on the electrode surface[20], which can block the active sites for HOR/HER. Even though no visible aggregates were observed on the µ-electrode surface, we cannot discard its formation.

Both in situ FTIR and SERS experiments show that (a trace amount of) water plays a crucial role. These experiments suggest that water is present at the Pt-acetonitrile interface initially, but is not observable until the oxidation current is flowing, in presence of molecular hydrogen. When H_2 is oxidized, the protons generated are preferentially solvated by water molecules, and leave the interface by migration of the solvated protons. Simultaneously, perchlorate ions migrate towards the surface. The SER spectra showed that the platinum oxides are formed

only in presence of water, at high positive potentials, and their formation is suppressed under hydrogen oxidation conditions.

The preferential solvation of protons by water in acetonitrile, leading to the migration of water away from the electrode surface once the protons are generated, is in good agreement with earlier conclusions about protons in acetonitrile-water mixtures. The preferential solvation of protons by water in water-acetonitrile mixtures follows from thermodynamic studies.[18, 21] Sublemontier and coworkers[5c] studied protons surrounded by solvent shells, following the mass spectra of supersonic beams containing hydrogen-bonded clusters of acetonitrile and water molecules. Their results showed that the protons, in presence of acetonitrile and small amounts of water, form solvation shells with the structure $(CH_3CN)_n(H_2O)_{n-2}H^+$. Furthermore, the stability of these clusters is granted by the formation of hydrogen bonds, and the arrangement of acetonitrile molecules in the outer coordination sphere is related to the acetonitrile as an acceptor of hydrogen bonds. A study by Benoit and Domain[22] reported the enthalpy of solvation of protons for several solvents, including water and acetonitrile. In their work, the heat of solvation for a proton in acetonitrile is -251 kcal.mol^{-1}, whereas for water it is -270 kcal.mol^{-1}. As stated by Burger,[23] these findings correlate well with the Gutmann donicities of both solvents (i.e. their ability to solvate cations) and endorse our observations of preferential solvation.

Regarding the low HOR currents registered in presence of Li^+ (see figure 1), we propose that the effect is related to the strong lithium-water interaction. Like protons, lithium is preferentially solvated by water in water-acetonitrile mixtures.[18] Water is a source of hydroxyl species, whose formation is promoted by the presence of Li^+.[20] As mentioned, in the presence of a larger amount of water in $LiClO_4$, a deposit was observed on the electrode surface. On the other hand, it has been reported[24] that the TBA^+ is solvated by acetonitrile; moreover, it can form hydrophobic clusters with the solvent, even at high water concentrations.

From our observations, we conclude that the hydrogen oxidation and evolution in acetonitrile are mediated by the presence of water, and this sensitivity towards the nature of the cations is attributed to preferential solvation effects. Therefore, we propose that the overall reaction of HOR/HER on platinum in acetonitrile should be written as:

$$H_2 + 2nH_2O(AN) \leftrightarrow 2H^+(H_2O)_n(AN) + 2e^- \quad \text{(Eq. 3)}$$

It is worth mentioning that the detailed structure of the solvation shells for the cations escapes the scope of this study. Like our present work, many previous reports on the HOR/HER on Pt in acetonitrile did not use rigorously water-free acetonitrile in combination with rigorously water-free electrolytes. In the light of our results, the practical meaning of the Hydrogen Electrode as a potential reference or activity benchmark in acetonitrile has its limitations because protons are preferentially solvated by water, at least under the experimental conditions described in this work. In general, the HOR/HER electrode kinetics in acetonitrile is highly sensitive towards the presence of water traces, even to the extent that purposefully adding water makes no apparent difference.

2.5. Conclusions

In this paper we studied the hydrogen oxidation and hydrogen evolution reactions on a platinum electrode in an acetonitrile-based electrolyte, by a combination of voltammetry and *in situ* Infrared and Raman Spectroscopy. From these spectroelectrochemical measurements in absence and presence of added water, we conclude that the hydrogen oxidation and evolution in acetonitrile is strongly mediated by (trace amounts of) water, as the protons generated by hydrogen oxidation are preferentially solvated by water. These water-carrying protons migrate away from the electrode surface during the anodic reaction. Therefore, the reversibility of HOR/HER in acetonitrile depends, to a certain extent,

on the solvation degree of the species involved in the electrocatalytic reaction, specifically on the presence of water. We also conclude that water is not involved in the electrochemical reaction, but it acts as a co-solvent to the cations in solution. This makes it difficult to establish a proper hydrogen reference electrode for non-aqueous solvents, and impacts on comparing catalysts of the HOR/HER reaction in different solvents. The implications of our conclusions could be extended to other systems under similar conditions, such as dimethylformamide and dimethylsulfoxide, which are also widely used in test systems for the development of new catalysts for hydrogen evolution.

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2.7. References

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