

Influence of alkali cations in the oxidation of glycerol on Pt and Au in alkaline medium

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Introduction

The understanding of the variables present in the mechanism electrocatalytic reactions requires knowledge of the nature of interactions between all species involved, i.e., anions and cations present in the electrolyte, reaction intermediates formed from the reactants and the reactant itself.

Recently, some studies have brought a new approach on the key issues present in these processes. Strmcnik *et al.*¹ have shown that non-covalent interactions between alkali metal cations and oxygen species adsorbed on Pt have a strong influence on the electrocatalytic properties of Pt for reactions present in the fuel cell. Sitta and coworkers², in accord with this work, reported the impact of the presence of cations of alkali metals (Li^+ , Na^+ and K^+) in the mechanism of electrooxidation of ethylene glycol on Pt. Although dealing with reactions onto Pt surface, these studies showed general insights which could be applied to other surfaces.

Considering the growing interest of several works performed in alkaline media, we propose study the influence of alkali metal toward glycerol electrooxidation reaction on gold and platinum electrode.

Experimental

All electrochemical measurements were carried out in conventional three-electrode glass cell. Pt and Au disks were used as working electrodes. A reversible hydrogen electrode (RHE) in the supporting electrolyte was employed as the reference electrode. Pt or Au wires were used as counter electrode. Appropriate amount of glycerol (JT Baker) was added to the alkaline solution to yield a glycerol solution containing 0.1 mol L^{-1} .

Results and Discussion

In Figure 1(a) are shown CV's for glycerol electrooxidation on Au and Pt electrodes in aqueous MOH (LiOH , NaOH and KOH) electrolytes. Regarding the question of the role of the cation, it is worth noting that the presence of them on the glycerol electrooxidation do not cause significant modifications on the CV's profiles. For Pt electrode, a clearly dissimilarity is present in the current peak density at positive scan, in other words, the presence of different cations in the electrolyte provokes a decrease of the density current as the charge density of the metal cation increase ($\text{Li}^+ > \text{Na}^+ > \text{K}^+$). When we turn our attention to the CV's for Au (red line) in the same electrolytes, they reveal that the current densities display great similarity (if we take into account only the influence of cations). These astonishing results reveal that, unlike platinum, gold is not affected by the presence of the alkali cations (Li^+ , K^+ e Na^+) toward glycerol catalysis reaction.

In order to shed some light to the voltammetric results a series of chronoamperometric measurements of the glycerol oxidation were performed for Pt and Au surfaces at different final potentials in KOH , NaOH and LiOH electrolytes. Potential pulses were applied from 50 mV to a desired potential in a range of $0.05 \text{ V} < E < 1.5 \text{ V}$ vs. SHE (data not shown). Based on these chronoamperograms, curves of current density versus the final potential reached ($j-E$) were constructed from the current density sampled at 30 seconds after the final potential was reached. The corresponding curves are shown in Figure 1(b).

We can note that at gold and Pt surface the current densities response are very analogous to the voltammograms. At Pt, the chronoamperometric, as displayed in the voltammograms, the Li^+ provokes a suppression of glycerol oxidation in contrast of the increase overall reaction rates as the alkali metal charge density increase. Some works reported that the alkali cation on the mechanism of the oxygen reduction^{1,3}, ethylene glycol² and methanol¹ electrooxidation reactions on Pt produce the same behavior that reported here: an increase in the overall reaction rates as the charge density of the alkali cation decrease. However, as we can note in Figure 1(a) and 1(b), a new feature of the role of alkali cations towards electrooxidation of small organic molecules on Pt, is not seen on gold surface.

Such behavior can be rationalized from two viewpoints: interaction between the cluster ($\text{M}^{+n}(\text{OH})_x$) and OH_{ads} and the effect of the potential. The first proposition is based on the fact that on gold the OH coverage is less than 0.2 ML and consequently the non-covalent interaction of the cluster and the gold modified surface is less pronounced than on platinum, which has approximately 0.7ML of OH_{ads} during the glycerol oxidation. On the other hand, we can take account that the potential range which the reaction takes place is distinct for both surfaces. On gold, the glycerol oxidation occurs at ~0.4 V higher than on platinum. It is expected that the cluster profile concentration ($\text{M}^{+n}(\text{OH})_x$) is function of the electric potential, and consequently, on gold, this concentration is considerably smaller than on platinum. The trend proposed could be the consequence of a fewer cluster cations non-covalent interactions with the gold surface which, in platinum, is greater. Then, we propose that at relatively more positive potential the non-specific interactions between the ions and alkaline solvated species OH_{ads} are less favored. This situation would provide a negligible influence of the cation in the reaction mechanism on gold.

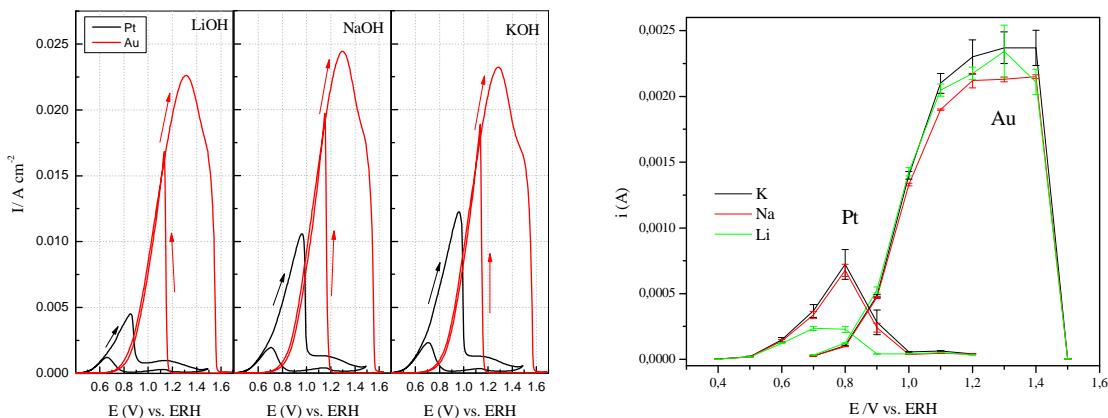


Figure 1: (a) Cyclic voltammograms of 0.1 mol L^{-1} glycerol oxidation on Pt (black line) and Au (red line) in 0.1 mol L^{-1} . Scan rate: 50 mV/s (b) Sampled current density vs. potential. The curves were constructed from current transients at sampling time of 30 s for different final potential.

Conclusions

In summary, the modified surface by OH and the potential applied at the electrode can not be analyzed separately when the presence of alkali metals are in the electrolyte. Probably, the electroactivity of such metals toward organic compounds oxidation involves a synergistic effect of given

References

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