Electro, Physical & Theoretical Chemistry

Alkali Cation Effect During the Oscillatory Electroreduction of H_2O_2 on Pt

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Hydrogen Peroxide Reduction Reaction (HPRR) catalyzed by Pt was studied in alkaline media and the effect of alkali cations were analyzed by the changes on dynamic instabilities presented by this system under high ohmic drop conditions. The origin of these instabilities is the competition between OH_2^- electroreduction and hydrogen adsorption on Pt surfaces, the latter being the first step for hydrogen evolution reaction (HER). Both HER and hydrogen adsorption are cation-dependent which suggests that noncovalent interactions are able to stabilize the water molecules favoring the Pt–H formation. Thus, in an interphase, in which the noncovalent interactions are more effective, HPRR will proceed as an indirect poisoned system, reflecting on slow frequency oscillations (ω), for instance $\omega_{LiOH} < \omega_{NaOH} < \omega_{KOH}$ for several H_2O_2 concentrations.

Hydrogen peroxide is an important molecule in several fields because its oxidation/reduction reactions are involved in biological, environment and energy storage systems.[1] Understanding the mechanism of its oxidation (to molecular oxygen – Hydrogen Peroxide Oxidation Reaction, HPOR) or reduction (to water – Hydrogen Peroxide Reduction Reaction, HPRR) will provide significant insights to design more efficient catalysts and sensors.[2]

Regardless the HPOR or HPRR processes, the system reaches the diffusion-limited current (DLC) condition until secondary electrochemical pathways, like oxygen or hydrogen evolution reactions, start to compete for active surface sites.[2a] At low potentials, this competition with H_{ad} can produce dynamic instabilities, observed as current or potential oscillations. The Pt/H_2O_2,H_2SO_4 system assigns an emblematic example of oscillatory electroreduction kinetics.[3]

The influence of halide ions, surface orientation and H_2O_2 concentration on these oscillations was extensively studied in the last two decades.[4] Recently, Mukoyama et al.[5] observed distinct kinds of potential oscillations, named H, I and J-type,

after the addition of Na^+ or K^+ ions in acid electrolyte, indicating the sensitivity of oscillations to weakly interacting species on surface. Indeed, cations effect on electrochemical systems has been easily recognized in alkaline media for several fuel cell reactions and connected with the interactions between hydrated cations and adsorbed species.[6] This effect modifies both shape and frequency of oscillations once the population of adsorbed species are affected by distinct cations as observed during ethylene glycol electro-oxidation on Pt.[6b,7] In alkaline media, the reduction reaction of HO_2^- (the deprotonated form of H_2O_2 in a chemical equilibrium step with pKa = 11.7) also depicts I and J oscillations[5b] but the effect performed by the cations is still unclear.

Herein, we analyse the effect of alkali cations, K^+, Na^+ and Li^+ on the current oscillations observed during HO_2^- electroreduction reaction in alkaline media at low H_2O_2 concentrations. Based on the accurate control of the ohmic drop between working and reference electrodes, the effective potential at the surface was calculated and the oscillations could be correlated with the processes in the absence of HO_2^-.

Figure 1 (a) shows cyclic voltammograms (CV) of a Pt microelectrode in the presence of 0.1 mol L^{-1} MOH (M=Li, Na or K) + 25 mmol L^{-1} HO_2^-. The current was normalized by the limit values at 1.2 V, that were ca. 10 mA cm^{-2} regardless the cation. At potentials higher than 0.8 V or between 0.30 and 0.70 V, oxidation and reduction currents on DLC condition were observed. This behavior under stagnant electrolyte is allowed due to both relatively low HO_2^- concentration and small electrode area, resulting in a hemispherical diffusion condition.[8] At negative scans, cathodic current peaks higher than DLC values are probably connected to the excess of HO_2^- on the interphase during the oxidation to reduction transition or the reduction of molecular oxygen, once the latter is a product of HO_2^- oxidation. The position of this peak is influenced by the cations due to the interaction of oxygenated species on the surface. Its tendency is in agreement with previous works.[9] Around 0.20 V a decrease in the reduction process is connected to the competition of H_{ad} for Pt sites, characterizing a negative differential resistance (NDR) region[3] that will be discussed below. According to the theoretical models, oscillations will be observed near NDR region if the total resistance exceeds a minimum value.[3,10]

Figure 1(b) brings the CV profiles after the insertion of 600 kΩ ohmic resistance and clearly the transition from oxidative to reductive process becomes wide but it is still possible to observe the DLC regions at sufficient high overpotentials. Moreover, current oscillations can be observed

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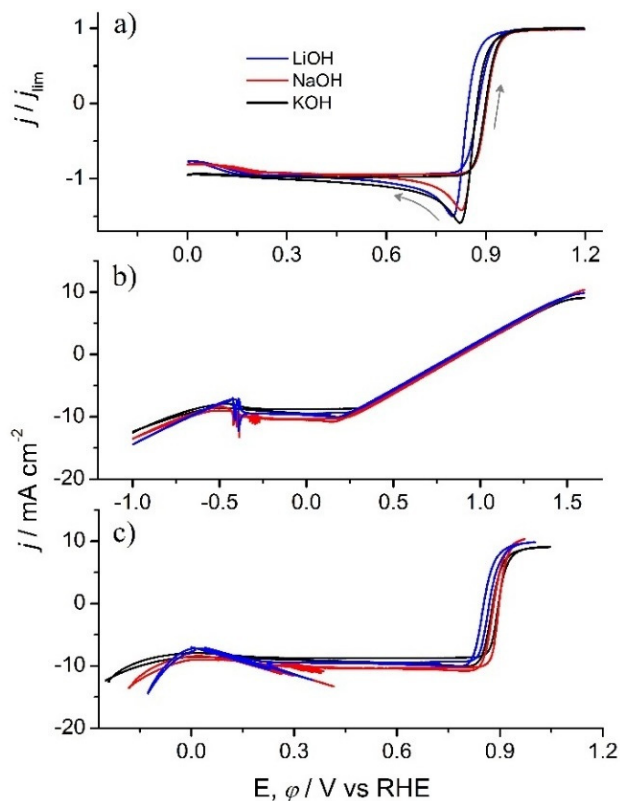Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.201702276

Figure 1. Cyclic voltammograms on Pt (microelectrode) at 0.05 V s^{-1} in 0.1 mol L^{-1} MOH (M=Li, Na or K) and 25 mmol L^{-1} HO$_2^-$ without (a) or with (b) the insertion of 600 kΩ. (c) current versus φ profiles. Arrows indicate the sweep direction.

Figure 2. Time series at E=-0.40 V in 0.1 mol L^{-1} MOH (M=K (a), Na (b) or Li (c)) and 25 mmol L^{-1} HO$_2^-$.

around – 0.4 V regardless the cations in the solution. The surface potential (φ) assumes different values of applied potential, due to the high ohmic drop, according to the equation: $E = \varphi + iR$. Hence, it is possible to calculate φ discounting the iR term. Figure 1(c) shows the same CV of panel (b) but in terms of φ, highlighting the connection between the oscillations and NDR region – after the correction they fall into the same potential window. Finally, the onset of hydrogen evolution reaction (HER) at negative potentials (versus a same solution reversible hydrogen electrode) are also affected by cations, i.e., the increase of cation's charge density lowers the overpotential to HER.[11] The position in which the oscillations appears in CV suggests they represent the I-type class.[5b]

The insertion of external resistances to trigger current oscillations allows us to precisely control the pre-treatment steps, once these steps can be done in condition of low ohmic drop, in which rigorously surface potential control is provided. Performing 5 cycles on the conditions of Figure 1(a), followed by insertion of a desired resistance and instantaneously measurement of CV's shown in panel (b), allowed us to collect very reproducible results.

The temporal behavior of oscillations can also be analyzed by fixing the potential at – 0.40 V after following the pre-treatment described above. Figure 2 depicts representative temporal patterns obtained in distinct supporting electrolytes
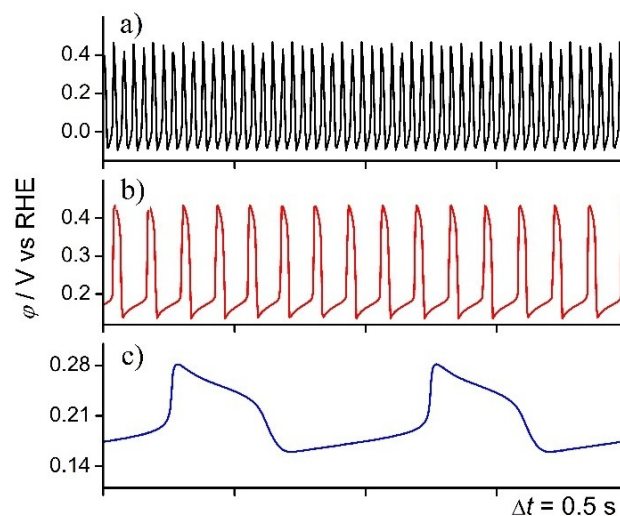
corrected by ohmic drop. It is well known in the literature that oscillatory H$_2$O$_2$/HO$_2^-$ reduction reaction displays a myriad of patterns depending on the employed experimental conditions.[4a,12] Even at fixed potential values, the patterns can be changed due to the evolution of uncontrollable variable as local potential/current fluctuations and changes in the population of intermediates covering the surface.[13] This strong sensitivity highlights surface changes sometimes not observable in classical electrochemical experiments. In the present work it was observed two distinct patterns named: *Period 1* (P1) and *Mixed Mode* (MM).[12] While in the presence of K$^+$, MM oscillations happens before P1; in the presence of LiOH, it was found the opposite order. For convenience, only P1 features will be discussed in this communication.

Remarkably, the oscillation frequency decreases 25 times from K$^+$ to Li$^+$ containing solutions, and the amplitude (peak to peak) increases in the opposite direction. Mukoyama et al.[4a,c] observed changes on the oscillation frequency, amplitude and patterns during the electroreduction of H$_2$O$_2$ in acid media in the presence of small amounts of halide ions – some classical spectators that compete to Pt sites.[14] The same dependence was found during methanol, formaldehyde and formic acid electro-oxidation reactions.[15] Considering the general mechanism to oxidation of small organic molecules,[16] the high adsorption strength of anions can direct compete with water and electroactive molecule adsorption, modifying the CO$_{ad}$ coverages – one of the key species responsible for the negative feedback loop in the oscillatory classical mechanism.[3,10] Herein, due to the potential in which oscillations are observed, Pt–H or Pt-H$_2$O are the two most probable species acting on surface[4a,5] together with HO$_2^-$ intermediates. It is unlike that the Pt–H is interacting with the cations due to the charge repulsion, therefore it is expected some interaction of cations with species involved in Pt–H formation or directly on the HPRR to trigger the behavior observed in Figure 2.

In alkaline media, Pt—H coverage is provided by water dissociation, (Reaction 1), that involves the adsorption of water molecules before yields Pt—H and OH⁻.[17] This water adsorption step is influenced by noncovalent interaction with cations[11a], dictating thus the Pt—H formation rate. Likewise, HO_2^- reduction, mediated by Pt active sites, involves water molecules (Reaction 2). In this scenario, water and Pt sites are common in both reactions, which can lead to the competition between them, resulting in the NDR behavior:

$$H_2O + Pt + e^- \rightarrow Pt-H + OH^- \qquad \text{Reaction 1}$$

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \qquad \text{Reaction 2}$$
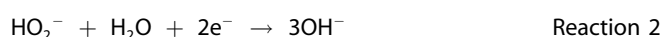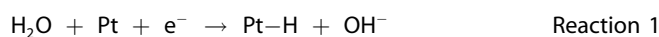
Considering the cations employed in this work, the non-covalent interactions strength with adsorbed species follow the order: $K^+ < Na^+ < Li^+$, once the cations have the same charge and the ionic radius increases from Li^+ to K^+. Both HER and NDR region, ca 0.2 V before HER onset, are cation-dependent (Figure 1) suggesting that the noncovalent interactions are able to stabilize the water molecules on the surface favoring the Pt—H formation. Thus, in an interphase in which the non-covalent interactions are more effective, like in the presence of Li^+, HPRR will be indirectly poisoned, reflecting on slow frequency oscillations when compared with the system composed by KOH supporting electrolyte. On the other hand, the HPRR also involves adsorbed oxygenates species, that could be interacting with electrolyte cations. HPRR can be modified by the presence of spectators (like H_{ad}, OH_{ad} or halide anions)[4d,12,18], however the cations seem to modify the HPRR only in regions in which H_{ad} or OH_{ad} (from water) are present, suggesting that the changes caused by cations on HPRR come mainly from the interactions with interfacial water instead of species from HO_2^- adsorption. Numerical experiments are in progress to understand this effect. The hydrolysis of cations, an important process in CO_2 reduction reaction[6d,e], was not considered here taking into account the distinct experimental conditions i.e. high potential and electrolyte pH.

The same trends were found to distinct HO_2^- concentrations, as tested for 20 and 30 mmol L⁻¹ and maintaining the ohmic drop constant, i.e. changing the external resistance in order to compensate the current-concentration dependence. Table 1 summarizes the mean oscillations frequencies obtained.

Table 1. Mean frequencies of P1 oscillations, in s⁻¹, according to the cations and HO_2^- concentration

	20 mmol L⁻¹	25 mmol L⁻¹	30 mmol L⁻¹
LiOH	0.53 ± 0.03	0.98 ± 0.06	1.35 ± 0.07
NaOH	1.45 ± 0.09	7.1 ± 0.7	7.4 ± 0.5
KOH	15 ± 3	25 ± 2	35 ± 3

Regardless the cation present in solution, the frequency of the oscillations increase with HO_2^- concentration, reaching 35 Hz in the presence of K^+, in agreement with results in rotating disc electrodes and acid media.[19] Remarkably, the same trend

caused by the cations observed in 25 mmol L⁻¹ is maintained and it can be explained by the actuation of HO_2^- on feedback cycles[3b]: HO_2^-/H_2O_2 is usually described taking part on negative (slow) feedback cycle in which the diffusion processes inside the Nernst diffusion layer are important. It is expected that increasing HO_2^- bulk concentration the entire oscillation cycle be restored fast, reflecting in a direct relation between HO_2^- concentration and mean oscillation frequency, as observed on Table 1.

In conclusion, the noncovalent interactions between cations and oxygenated species play a significant role in the electrocatalysis of several systems, in this work the effect were analyzed to the hydrogen peroxide reduction reaction at constant ohmic drop. Due to the competition for active sites between hydrogen formed from dissociation of water molecules and HO_2^- species, there is a negative differential resistance region, in which it is possible to observe oscillatory kinetic. Besides that, the stability of oxygenated species is influenced by alkaline cations reflecting in distinct oscillations frequencies. The strength of these interactions should follow the order $K^+ < Na^+ < Li^+$, once the cations have the same charge and the ionic radius increases from Li^+ to K^+, reflecting in oscillations frequencies about 25 times lower in the presence of Li^+ when compared to K^+. The behavior was interpreted as an indirect poisoning effect caused by the first steps of hydrogen evolution reaction once the latter is catalyzed in the presence of Li^+.

Supplementary Information Summary

Experimental details are provided in supplementary section

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Cation Effect · Competition on Surface · H_2O_2 Electroreduction · N- NDR oscillator · Oscillations

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