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Influence of the electrolyte composition on the activity and selectivity of electrocatalytic centers

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ABSTRACT

The capability to efficiently design new electrocatalytic materials depends on a deeper understanding of all factors influencing the performance of active sites under reaction conditions. While the electrode surface structure and composition are primary, the role of electrolyte components in the activity and selectivity of catalytic centers is also significant, if not drastic. Interestingly, the performance of electrocatalysts is not only affected by the so-called specifically adsorbing ions. Many species, which are generally considered "inert", can *de facto* change the key properties of the catalytic sites. However, the origin of such experimentally observed effects is often poorly understood. Despite the fact that certain trends are frequently observed, further investigation of model systems and development in the field of quantum chemistry calculations are necessary in order to gain deeper insight into the effects of the electrolyte composition. The goal of this review article is to summarize and analyze recent achievements in the elucidation of the non-trivial effects of electrolyte components and their contribution to the observed performance of catalytic centers. A particular focus is set on the influence of (i) alkali metal cations, (ii) commonly used anions, (iii) unexpected pH effects, as well as (iv) the impact of certain ionic liquids on the activity and selectivity of catalytic systems. Reactions which are essential for the prospective sustainable energy provision schemes are selected as illustrative examples.

1. Introduction

The main focus of electrocatalysis nowadays is to find relatively simple rules explaining complex interactions between reaction intermediates and the electrode surface, which are responsible for the activity as well as selectivity observed in catalytic systems [1–12]. While common concepts and paradigms are quite similar in both classical heterogeneous catalysis and electrocatalysis [13,14], there is at least one peculiarity that additionally complicates understanding and design of new electrocatalytic systems. The distinction is that the catalytic processes occur at the electrified interface, where the contribution of all charged species located in the close proximity to the active centers cannot be ignored [15–20]. They often include supposed "spectator species", which should be distinguished from those recognized as reaction intermediates. As a first approximation, these species are not expected to influence the electrocatalytic reactions [21–23]; and this is the main reason why they are used as the components of supporting electrolytes. The latter are normally designed to provide a reasonably high ionic conductivity. However, it looks like many of those commonly used electrolyte constituents markedly contribute to the properties of active sites [24,25].

Recent experimental observations suggest that the role of numerous supporting electrolytes in catalysis has probably been underestimated if not sometimes ignored for a long time [26–31]. Moreover, with the development of new experimental protocols, a variety of non-straightforward effects caused by the electrolyte composition on activity and selectivity cannot be explained by e.g. just a presence of "unknown contaminations" or other purely side issues.

Experimental and theoretical investigations of interactions between the spectator species and active sites are, however, frequently complicated because of their intrinsic dynamicity. Classical surface science techniques often fail in providing clearly interpretable in situ information for the particular cases of the electrochemical interface. On the other hand, the framework of the theoretical quantum chemistry calculations is in many cases

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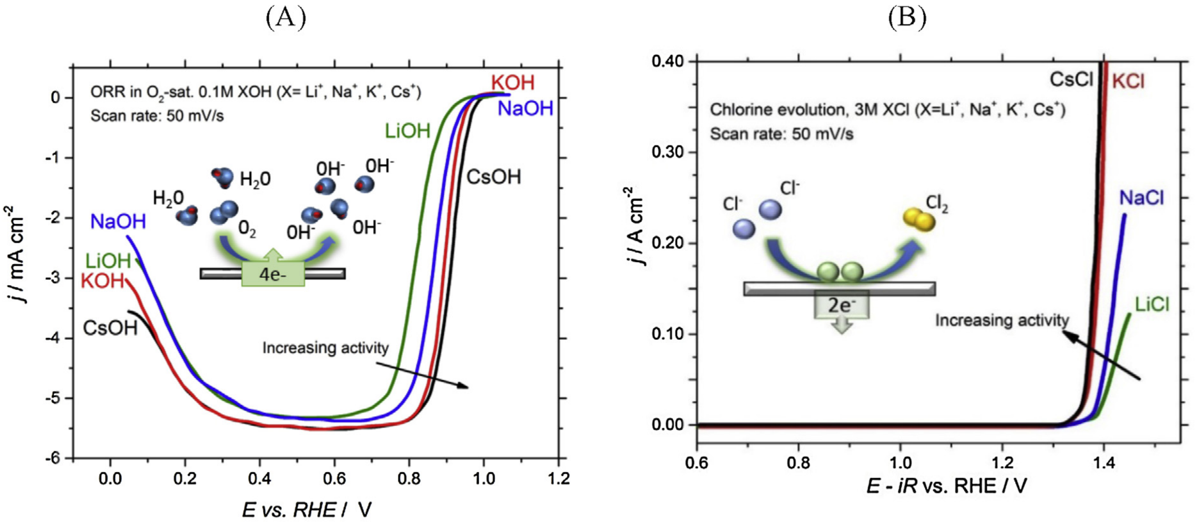

Fig. 1. The effect of alkali metal cations on the electrocatalytic activity of Pt electrodes with different surface status. (A) Voltammograms for the oxygen reduction reaction on Pt(1 1 1) in O_2 saturated 0.1 M XOH (X = Li, Na, K, Cs); original data are from Ref. [44]. (B) Voltammograms characterizing the chlorine evolution reaction on polycrystalline Pt/PtO_x in the presence 3 M XCl (X = Li, Na, K, Cs) in HCl, pH 2; original data are from Ref. [47].

either “too static” or “too fast” to give a deeper insight into these interactions.[1] Nevertheless, recent experimental results and existing theoretical models suggest that the variation of the electrolyte composition can be considered as an additional degree of freedom in designing of efficient electrocatalytic systems [32–35].

This review article focuses on several topics which are related to the effect of the electrolyte composition: Section 2 analyses the role of the alkali metal cations, Section 3 deals with interplay between pH, anion and cation effects, and Section 4 considers selectivity and activity aspects related to the use of ionic liquids in electrocatalysis. Further possible directions toward the design of new systems are also briefly outlined.

2. Influence of the alkali metal cations

Aqueous solutions containing alkali metal cations are among the most widely used electrolytes. Not only laboratory experiments are regularly performed in the presence of, e.g. Na^+ or K^+, but they are constituents of working media for industrial synthesis of, for instance, pure H_2 [36] or in the large-scale production of gaseous Cl_2 [37]. Remarkably, observations that the nature and the concentration of these spectator species influences many electrode processes have been reported, as perhaps, early as in the 1930s. One can, for instance, admit some observations of Herasymenko and Slednyk [38], who reported that the hydrogen overpotential on mercury electrodes was dependent on the nature and concentration of supposedly “inert” cations (namely Li^+, Na^+, K^+, Rb^+, La^{3+}, and Th^{4+}). Shortly after that, Tokuoka [39] observed that the rates of electroreduction of $XO_3{}^-$ type anions (e.g. $NO_3{}^-$, $BrO_3{}^-$ and $IO_3{}^-$) were substantially influenced by a hypothetical adsorption of cations (e.g. Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, La^{3+}). This subject has, however, drawn relatively modest interest ever since, despite the fact that some remarkable persons, for instance Heyrovsky or Frumkin, suggested its great importance [40–43].

Since that time, the focus has been strictly shifted toward the electrode materials. The electrode structure and composition are indeed, in the majority of cases, the most prominent factors in electrocatalysis. Therefore, many cations such as those of alkali metals were frequently considered as just inert spectator species with a negligible intrinsic influence on the electrode processes.

However, with further advancements in experimental methodologies and with the better fundamental understanding of electrocatalytic processes, the influence of alkali metal cations has again attracted great attention involving a wide range of environments [44–52]. It is now clear that considering only the electronic properties of the surface is probably not enough to describe or predict the performance of this kind of systems in detail. One illustrative example is given in Fig. 1: Pt and Pt/PtO_x electrodes have been used for the oxygen reduction reaction (ORR) and chlorine evolution, respectively. One can clearly see in the Figure that the influence of alkali metal cations on substantially different electrocatalytic reactions is significant.

Specifically, Fig. 1A demonstrates that the activity of Pt(1 1 1) electrodes toward the ORR increases in presence of alkali metal cations in the following order: $Li^+ < Na^+ < K^+ < Cs^+$, i.e., it obviously changes with the rise of the radius of the cation. The same trend is valid for the anodic chlorine evolution at the very different pH and drastically dissimilar status of the Pt electrodes (metal vs. metal-oxide surface and monocrystalline electrodes vs. polycrystalline ones), as illustrated in Fig. 1B.

One possible explanation of this kind of behavior would be based on the formation of envisaged dynamic X(H_2O)-adsorbate structures in the close proximity to the surface. Since the hydration energy increases in the order $Cs^+ > K^+ > Na^+ > Li^+$ [53], the formation of the above-mentioned complexes could also result in some consistent trends (in the same order) in the stability of those structures or complexes at the electrode surface [44,48,54]. However, it is probably not straightforward to elucidate the exact activity trend in the variety of cases. For the oxygen electroreduction, one possible explanation accounts for the OH_{ads}–Pt interaction (OH_{ads} is a key ORR intermediate), which is mainly determined by the apparently high density of charge between the surface and the cations. The decrease of this charge density accompanied by the increase of the OH_{ads}–Pt distance is suggested to stabilize the adsorbate. Ions such as Li^+ can likely polarize the adsorbed hydroxyl to a higher degree, reducing the charge density between the Pt electrode and OH_{ads}. This might stabilize the envisaged complexes. The stabilized OH_{ads}, in turn, acts as a bystander and, therefore, blocks the active

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[1] With the current state-of-the-art, this roughly corresponds to the thermodynamic or molecular dynamic simulations, respectively.

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