Electrochemistry Communications 63 (2016) 1–4

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

Impact of the alkali cation on the electrocatalytic oxidation of urea and benzyl alcohol on nickel electrode

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ARTICLE INFO

Article history:
Received 6 November 2015
Received in revised form 1 December 2015
Accepted 1 December 2015
Available online 9 December 2015

Keywords:
Alkali metal cations
Urea
Benzyl alcohol
Nickel oxyhydroxide
Electro-oxidation

ABSTRACT

The effect of electrolyte alkali metal cations (Li^+, Na^+, or K^+) on the electro-oxidation of urea and benzyl alcohol on NiOOH catalyst has been investigated by means of cyclic voltammetry and chronoamperometry in the presence of an electrolyte containing LiOH, NaOH, or KOH. The catalytic activity toward the electro-oxidation of urea and benzyl alcohol was found to increase in the sequence $Li^+ < Na^+ < K^+$. This activity's difference is partly caused by different surface blockage abilities by $OH–M^+(H_2O)_x$ (M: Li, Na, K) clusters, which is similar to many electrocatalytic reactions on Pt reported previously, additionally, incorporation of various cations to the catalyst may induce the activities difference as well.

1. Introduction

The relationships between the electrode surface structure or composition and the apparent catalytic activity are usually the main research topics in the studies of electrocatalysis. However, recent experimental results verified that the electrocatalytic activity can be significantly influenced by electrolyte components [1]. Aqueous solutions including alkali metal cations have been widely used in many electrocatalytic reactions toward lots of small molecules, in particular, influence of the alkali metal cations on the activity as well as selectivity has been carefully examined among them. For example, in studies of electrocatalytic fuel cell reactions on platinum, Markovic *et al.* demonstrated that the activities of the oxygen reduction reaction, the hydrogen oxidation reaction, and the oxidation of methanol decreased from CsOH to LiOH($Cs^+ > K^+ > Na^+ >> Li^+$); this phenomenon was rationalized in terms of different non-covalent force between $M^+(H_2O)_x$ and PtOH at electrode interface [2]. Similar behaviors have been observed in the electrocatlytic oxidation of carbon monoxide [3], formate ions [4], ethylene glycol [5], and hydrogen peroxide [6] on platinum. However, it has been explored that electrocatalytic activities for the methanol and ethanol oxidation reactions on Au(111) are independent of the alkali metal cations [7], which is different from the case of Pt. Moreover, Li *et al.* found that TiO_2-based photoelectrodes in strong alkaline electrolytes show an abnormal trend of LiOH > KOH > NaOH in water oxidation activities [8].

It is well known that the $Ni(OH)_2$/NiOOH redox couple [9–11] can be used as an efficient redox mediator in many indirect electrocatalytic reactions including water splitting, urea decomposition, alcohols oxidation, and glucose detection [12–15]. The influence of metal cations such as Li^+, Co^{2+}, or Fe^{3+} on the electrochemical behaviors of positive electrode in Nickel-based batteries has been extensively investigated [16]. To our best knowledge, the influence of various alkaline cations on activities of NiOOH-mediated electrocatalytic oxidation reactions is still scarce; Kitchin *et al.* reported very recently that when using NiOOH as an electrocatalyst in oxygen evolution reaction, activities showed a trend of $Cs^+ > K^+ \approx Na^+ \approx Li^+$ in purified electrolyte and a trend of $K^+ \approx Na^+ > Cs^+ > Li^+$ in Fe-saturated electrolytes [17]. In order to gain more understanding in the electrolyte selection of NiOOH-mediated electro-oxidation reaction, the effect of the alkali cations on the electrocatalytic oxidation reaction of urea and benzyl alcohol mediated by NiOOH in aqueous KOH, NaOH, and LiOH solutions has been investigated using electrochemical techniques including cyclic voltammetry and chronoamperometry in this communication; electrocatalytic activities in these three electrolytes were compared and discussed.

2. Experimental

Cyclic voltammetry and chronoamperometry experiments were performed by an LK2006A electrochemical workstation (Lanlike,

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http://dx.doi.org/10.1016/j.elecom.2015.12.004
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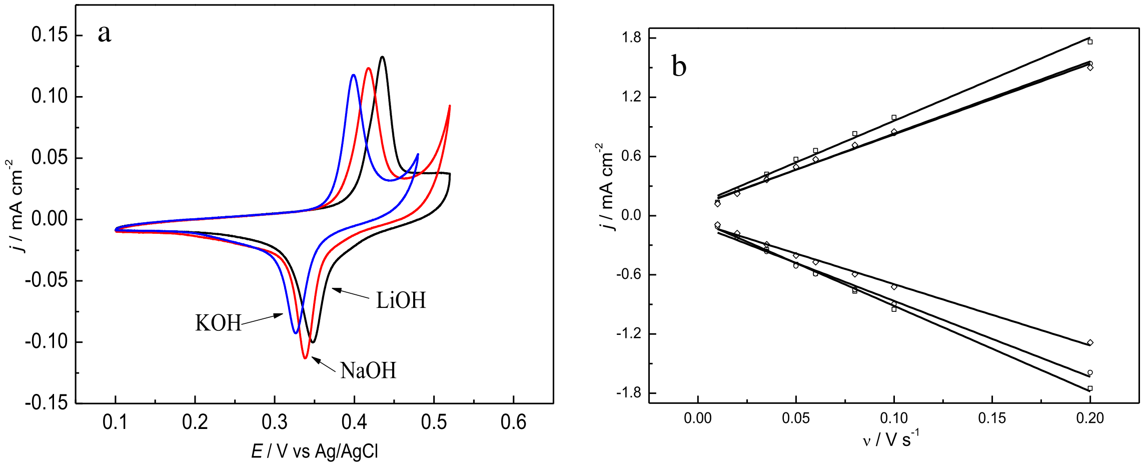

Fig. 1. (a) Cyclic voltammograms at 10 mV s^{-1} of nickel in 1 mol L^{-1} KOH, NaOH, and LiOH solution. (b) Dependency of anodic and cathodic peak currents on square root of scan rates in 1 mol L^{-1} KOH(□), NaOH(○), or LiOH(◇).

China) in a standard three-electrode electrochemical cell; iR compensation was carried out in all voltammetric experiments. The nickel films were used as the working electrode, whereas Ag/AgCl (with 3.5 mol L^{-1} KCl) and platinum plate served as the reference and counter electrodes, respectively. Similar to those previously reported [18,19], films of nickel were electrodeposited from 1 mol L^{-1} $NiSO_4$ and 0.5 mol L^{-1} H_3BO_3 on the copper electrode(3 mm diameter) under a potential of −1.25 V for 60 s. All chemicals were ordered from aladdin (Shanghai, China) and used without further purification. All solutions were prepared with ultra-pure water (18.2 MΩ cm). The electrolytes used were 1 mol L^{-1} hydroxide solutions of alkali metals (KOH, NaOH, or LiOH with high purity).

3. Results and discussion

CVs of electrodeposited nickel electrodes in aqueous MOH (M = Li^+, Na^+, K^+) are shown in Fig. 1a. It is obvious that the cathodic and anodic peak potentials of spontaneous formed $Ni(OH)_2$ shift to positive slightly in the three alkali metal hydroxides with an order of KOH < NaOH < LiOH, which is also evidenced by Anaissi et al. [20], variation of potentials in these three electrolytes might be caused by the possible interaction between OH^- and alkali metal cations. A scan rate study was carried out to understand the electrochemical behavior of oxidized Ni films in strong alkaline medium, and scan rates dependent cathodic and anodic peak currents are shown in Fig. 1b. A linear relationship can be observed in Fig. 1b at scan rates from 10 to 200 mV s^{-1}, which suggests an electrochemical activity controlled by surface-bound redox species ($Ni(OH)_2$ and NiOOH), and current densities are very low compared to the case of diffusion controlled. Meanwhile, peak-to-peak potential separations in these three alkali electrolytes are close; there are 87 mV, 80 mV, and 73 mV for 1 mol L^{-1} LiOH, NaOH, and KOH at scan rate 10 mV s^{-1}, respectively.

Fig. 2 compares the CVs of nickel films modified copper in 1 mol L^{-1} MOH (M: Li, Na, K) in the presence of 80 mmol L^{-1} urea or benzyl alcohol at scan rate 10 mV/s, and it clearly proves that catalytic activities of urea and benzyl alcohol electro-oxidation in nickel films follow the trend of LiOH < NaOH < KOH by comparing electrocatalytic peak current densities collected under the same experimental conditions. Additionally, Fig. 2 indicates that urea/benzyl alcohol molecules adsorbed on the electrode surface are oxidized at higher potentials compared to the oxidation of $Ni(OH)_2$ to NiOOH. Since a crossing loop from cyclic voltammogram can be used as a universal criterion for electrochemical oscillatory systems [21], the oscillatory electro-oxidation of urea on Ni catalyst in LiOH solution is predicted to be most insignificant due to its barely seen crossing loop in comparison with that in both KOH and NaOH medium (Fig. 2a). It should be kept in mind that Varela et al. reported the impact of the alkali cation on the oscillatory electro-oxidation of ethylene glycol on platinum [22], the oscillation frequencies decreasing in the order KOH > NaOH > LiOH has been shown and it is mainly explained in terms of the different strength of non-covalent interactions between PtOH and $M^+(H_2O)_x$.

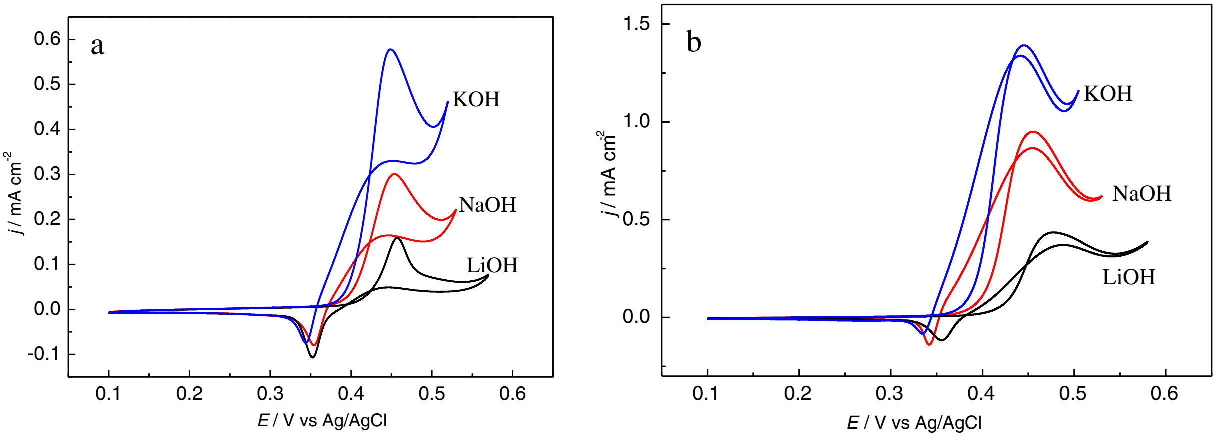

Fig. 2. (a) Cyclic voltammograms of nickel electrode in 1 mol L^{-1} alkaline solutions in the presence of 0.08 mol L^{-1} urea (a) and benzyl alcohol (b).