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Stability of Ni and Ti in Hydrogen Evolution in the Presence of 1-Butyl-3-methylimidazolium Tetrafluoroborate

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Ni and Ti electrodes were tested for hydrogen evolution reaction in water electrolysis using electrolytes containing 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM·BF_4) ionic liquid. Reductive currents of Ni and Ti at low potentials in BMIM·BF_4 (12 wt%) and KOH (6 wt%) aqueous electrolytes originate from hydrogen evolution with considering the electrolyte composition and the electrochemical window of the ionic liquid, which was confirmed by Pt electrode. While the Ti electrode shows a similar hydrogen evolution activity to the Ni electrode in the BMIM·BF_4 aqueous electrolyte, its activity is inferior to the Ni electrode in the KOH aqueous electrolyte without the ionic liquid. The existence of the ionic liquid in aqueous electrolyte appears to change the hydrogen evolution kinetics at both Ni and Ti electrodes as seen in Tafel analysis. This is partly because BMIM·BF_4 is susceptible to hydrolytic decomposition of $BMIM^+$ owing to the hydrogen at C2 position and of BF_4^- incurring HF formation. A measurement of electrode weight loss after a potentiostatic experiment and an accompanying SEM analysis indicate the surface roughening of the electrodes and the pore formation on the surface of Ti in the presence of BMIM·BF_4. This change in surface morphology can be attributed to HF that could be formed from the hydrolytic instability of BMIM·BF_4.

Keywords: hydrogen evolution, corrosion, ionic liquid, titanium, nickel

1. INTRODUCTION

Ionic liquids are room-temperature molten salts in the liquid state. While ordinary liquids such as water are predominantly made of electrically neutral molecules, ionic liquids are largely made of ions and short-lived ion pairs. They are widely used in electrochemistry due to their unique properties such as good ionic conductivity, wide electrochemical potential window, high thermal stability, wide liquid range and tunable solvent properties. In particular, ionic liquids are likely to be important in the field of energy including hydrogen-based fuel cells and so on [1]. One of the applications emerging in recent years is hydrogen production in water electrolysis [2-5]. Although water electrolysis for hydrogen production is one of the easiest and well-known methods, its usage is often limited to small scale and specialized situations where an access to large scale hydrogen production plants is not possible or economical mainly because hydrogen can be produced more affordably and economically from fossil fuel reforming. However, the recent, excessive rise in fuel price and the global environmental regulations make the water electrolysis attractive compared to the fossil fuel reforming due to its advantages as follows: no carbon emissions; ultra high-purity hydrogen production; sustainable and renewable fuel supply.

Metal electrodes are normally adopted for the hydrogen evolution reaction in water electrolysis. Platinum, among pure single metal elements, shows the best catalytic activity for hydrogen evolution with the highest exchange current density, which is equivalent to the smallest overpotential [6]. Platinum still proves to be the best catalyst for hydrogen evolution using ionic liquids as electrolytes [7]. However, mainly because of the prohibitively high Pt price, nickel is often used as a practical electrode material for hydrogen evolution due to its comparable stability and activity to Pt not to mention its reasonable price [8]. Although Ni itself shows a moderate cathode performance in a concentrated alkaline electrolyte, which is a usual choice in water electrolysis and provides a corrosive environment, Ni electrode modifications have been conducted by incorporating other transition metals such as Ti in a form of composites or alloys for a better catalytic activity and stability [9-12]. Titanium, of which most useful properties are known for corrosion resistance and the highest strength-to-weight ratio of any metal, has been tried to modify Ni electrodes in alkaline electrolytes but has not been tested in electrolytes containing ionic liquids. While the electrodeposition of Ti in ionic liquids has been often conducted as studied by Endres et al. [13], an investigation on the activity for hydrogen evolution reaction and the stability of Ti in water electrolysis containing ionic liquids has not been reported so far to the best of our knowledge. Incidentally, the material corrosion properties in the presence of ionic liquids are known to be different from those found in conventional electrolyte environments [14]. Therefore, it should be informative to compare the activity for hydrogen evolution reaction and the corrosion behavior of Ni and Ti in aqueous electrolytes including an ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate ($BMIM\cdot BF_4$)), which has good solubility with water at room temperature [15].

2. EXPERIMENTAL

The $BMIM\cdot BF_4$ ionic liquid was purchased from (C-tri) and was vacuum-dried before use. The aqueous electrolytes were prepared by dissolving the ionic liquid or by diluting KOH (85%, Dejung Chemicals) in distilled water. Two compositions of electrolytes of which ionic conductivity is similar were studied: $BMIM\cdot BF_4$ (12 wt%) in H_2O and KOH (6 wt%) in H_2O. The water electrolysis was performed using a Hofmann voltameter equipped with a metal working electrode, a Pt quasi-reference electrode (PtQRE) and Pt wire counter electrode [5]. Three kinds of metal electrodes were studied: Pt

(99.9%, Sigma-Aldrich), Ni (99.9%, Nilaco) and Ti (99.9%, Nippon Steel). The electrode surfaces were polished with sandpaper (1200 grit) and washed with commercial acetone. The electrode area submerged in the electrolyte solution was determined geometrically. The electrolysis potential was controlled with a potentiostat (Solartron 1287). Cyclic voltammetry, linear sweep voltammetry and potentiodynamic experiment for Tafel slope analysis were conducted at a scan rate of 10 mV/s. Potentiostatic experiment at -1.7 V was carried out for 30 min or 60 h. The potentials throughout this study are reported with respect to the PtQRE. The temperature was measured with a thermocouple during the electrolysis period and controlled with a circulating fluid thermostatic bath. The conductivity of electrolytes was measured using a Digimed-31 conductimeter using thermostated cells at room temperature. Changes in surface morphology of the metal electrodes after the potentiostatic experiment were observed with a scanning electron microscope (JEOL JSM-6500F).

3. RESULTS AND DISCUSSIONS

The stable electrochemical window of the employed ionic liquid was confirmed with Pt electrode in the ionic liquid electrolyte as in figure 1(a). There is no substantial reductive current flowing at as low as -2 V and this is in accordance with other reports where the electrochemical window of BMIM·BF_4 is about 4.3 V (+1.8 V to -2.5 V vs. PtQRE) [16,17]. The initiation of reductive current around -2 V might originate from the reduction of $BMIM^+$ with succeeding reactions of dimerization and de-alkylation [17]. Figures 1(b) and (c) show reductive currents of Pt electrode in BMIM·BF_4 (12 wt%) and KOH (6 wt%) aqueous electrolytes respectively. The reductive currents should result from hydrogen evolution reaction with considering the water content of electrolytes and the electrochemical window of the ionic liquid. Although Pt is a catalytic substrate that shows a negligible overpotential in hydrogen evolution, there appears a difference in onset potential of hydrogen evolution by several hundred mV depending on the kind of electrolyte. This is certainly not attributed to an intrinsic property of the electrolytes but to the pH-dependence of the reference electrolyte. Because the two electrolytes have different pHs (BMIM·BF_4 (12 wt%) electrolyte is acidic and KOH (6 wt%) electrolyte is basic), it might be inappropriate to compare each result on the same reference electrode basis. Besides, PtQRE is reported to be seldom reliable in some cases and different types of reference electrode such as Ag/Ag^+ micro-reference electrode were introduced recently [7,18]. Hereafter we will compare the overpotential of Ni and Ti with respect to Pt, which shows a negligible overpotential in hydrogen evolution, in the respective electrolyte to circumvent the strict adoption of reference electrode.

Figure 2 compares the electrochemical behaviors of Ni and Ti electrodes in BMIM·BF_4 (12 wt%) aqueous electrolyte. If an onset potential for hydrogen evolution is chosen arbitrarily as a potential where a reductive current density reaches -0.002 A/cm^2, a twentieth part of maximum reductive current density of Ni, Ni and Pt (as seen in figure 1) have the almost same hydrogen evolution onset potential around -1.1 V.

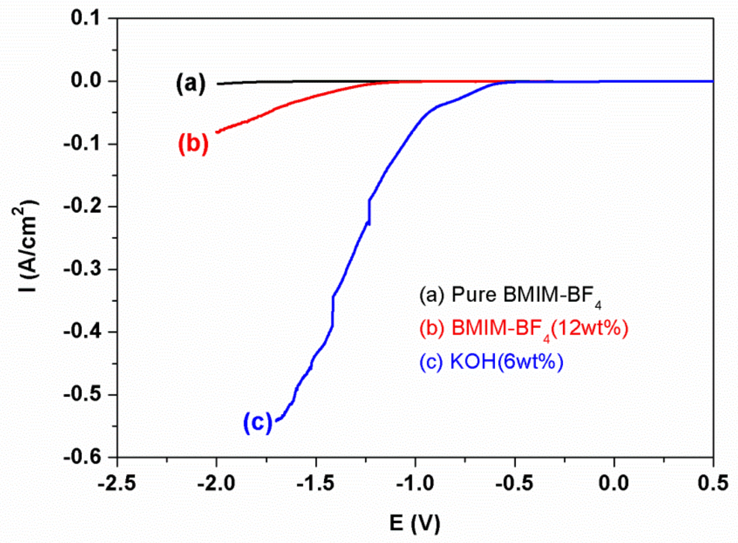


Figure 1. Linear sweep voltammogram of Pt in (a) pure BMIM·BF$_4$, (b) BMIM·BF$_4$ (12 wt%) and (c) KOH (6 wt%) aqueous electrolytes with a scan rate of 10 mV/s.

This is on a par with the onset potential for hydrogen evolution to those of Pt and Ni under the similar experimental condition of ionic liquid concentration (10 vol.% BMIM·BF$_4$), which was reported by de Souza et al. [3]. On the other hand, Ti has a lower onset potential of -1.7 V in spite of a relatively rapid increase in reductive current after the onset potential. It might be concluded that the catalytic activity for hydrogen evolution at Pt and Ni is on the same level followed by Ti in the presence of BMIM·BF$_4$ in water. Incidentally, the superior hydrogen evolution performance of Pt and Ni to Ti was also observed in another type of ionic liquid electrolyte (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) [7].

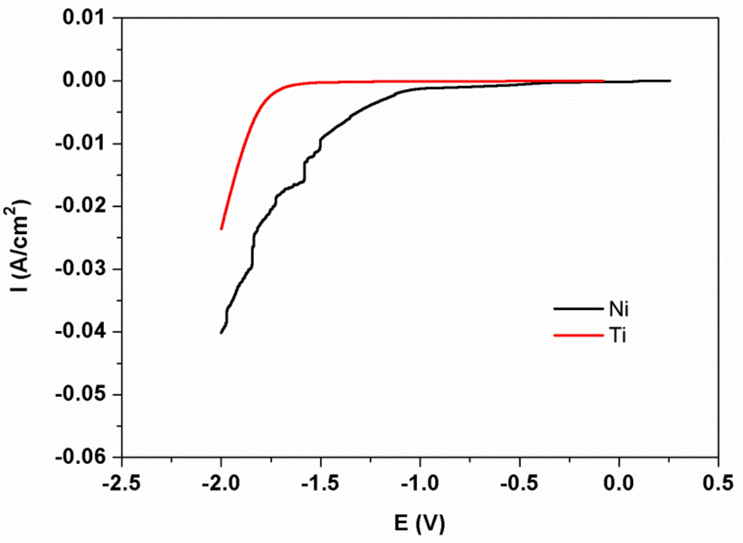


Figure 2. Linear sweep voltammogram of Ni and Ti electrodes in BMIM·BF$_4$ (12 wt%) aqueous electrolyte with a scan rate of 10 mV/s.

Figure 3 compares the electrochemical behaviors of Ni and Ti electrodes in KOH (6 wt%) aqueous electrolyte excluding the ionic liquid. Similarly when an onset potential for hydrogen evolution is chosen as a potential where a current density reaches a twentieth part of maximum reductive current density of Ni, Ni and Pt (as seen in figure 1) have the almost same onset potential around -0.7 V. Contrary to the aqueous electrolyte containing the ionic liquid, the overpotential for hydrogen evolution at Ti in the KOH aqueous electrolyte is larger by a small margin (ca. 120 mV) compared to Ni and Pt. Therefore, it would be safe to say that Ti has a more or less similar hydrogen evolution catalytic activity to Ni in alkaline electrolyte, which rationalizes the aforementioned attempts of Ni modification incorporating Ti for hydrogen evolution reaction in alkaline electrolyte [9-12].

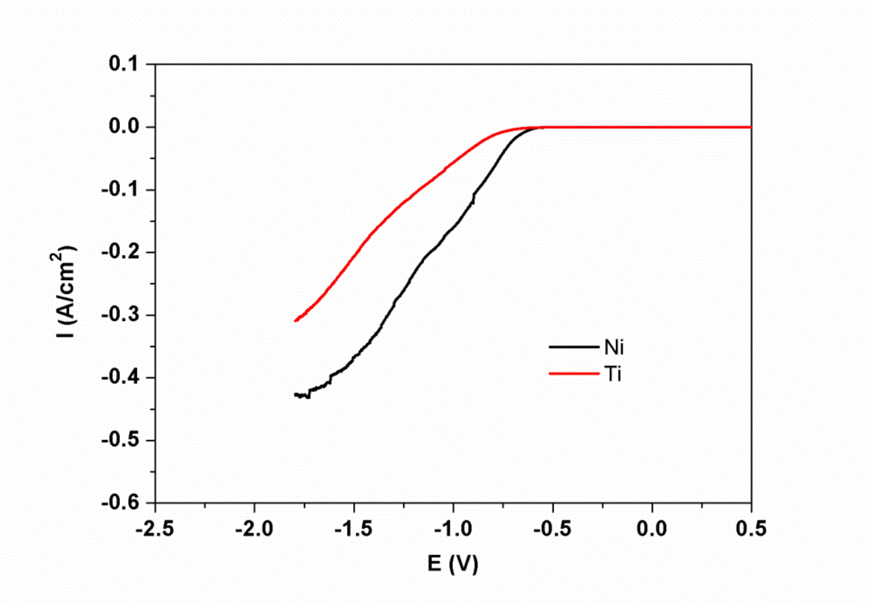


Figure 3. Linear sweep voltammogram of Ni and Ti electrodes in KOH (6 wt%) aqueous electrolyte with a scan rate of 10 mV/s.

Figures 4 and 5 are the polarization curves for cathodic current density region to figure out Tafel slopes of the electrodes. There are two distinct linear regions whose linearity is maintained for longer than one decade of current density in the presence of the ionic liquid in contrast with the KOH aqueous electrolyte case where only one Tafel slope is observed. The dual Tafel slopes in the presence of BMIM·BF_4 might result from the different source of proton donor: One is, without doubt, from hydrogen of water but the other is difficult to point out. The other proton source could be hydrogen attached to C2 of the imidazolium ring or other hydrogen-containing decomposition products of BMIM·BF_4 [5,19,20]. While only the simple dissociation of KOH is expected in KOH aqueous electrolyte with resulting in the common Tafel slope of ca. 0.12 V/dec for Ni and Ti, the hydrolytic instability of BMIM·BF_4 makes the solution chemistry of BMIM·BF_4 aqueous electrolyte complicated. In particular, BMIM·BF_4 is known to be susceptible to hydrolytic decomposition of $BMIM^+$ owing to the hydrogen at C2 position and of BF_4^- incurring HF formation [15,17,20,21]. Although the Tafel slope values themselves might need to be more elaborated, it is evident that the presence of the ionic liquid alters and makes the hydrogen evolution kinetics of the electrodes complicated.

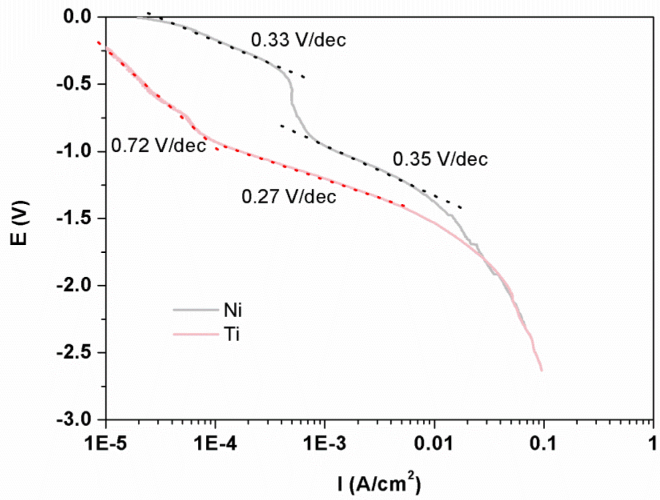


Figure 4. Polarization curves of Ni and Ti electrodes in BMIM·BF_4 (12 wt%) aqueous electrolyte with a scan rate of 10 mV/s for Tafel slope analysis.

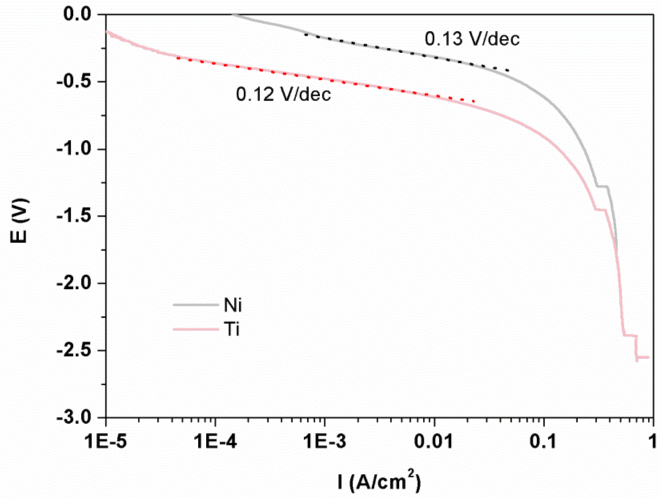
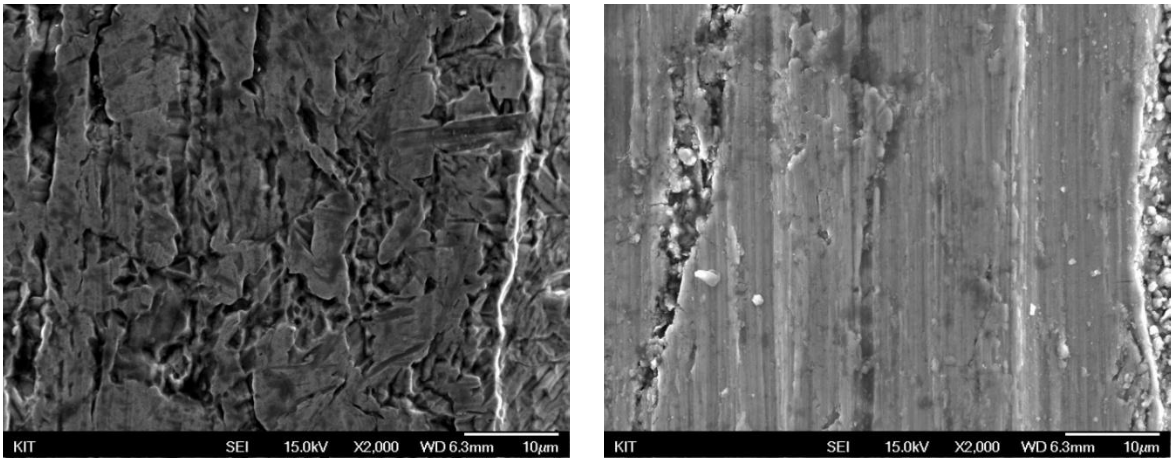


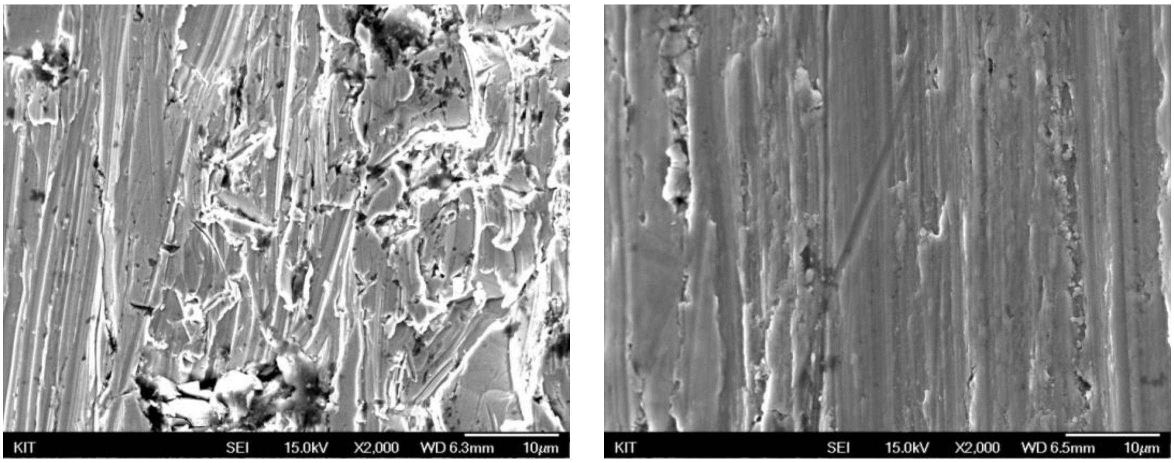
Figure 5. Polarization curves of Ni and Ti electrodes in KOH (6 wt%) aqueous electrolyte with a scan rate of 10 mV/s for Tafel slope analysis.

The stability of metal electrodes should be considered for the practical application to water electrolysis. Figure 6 illustrates changes in surface morphology of Ni and Ti electrodes before and after potentiostatic experiments (at -1.7 V for 30 min) in BMIM·BF_4 and KOH aqueous electrolytes. Overall, the electrodes appear more roughened in the presence of BMIM·BF_4 than KOH. Further, small pits or pores seem to develop during the potentiostatic experiments more prominently in the presence of the ionic liquid, however, which makes the observation of pores more difficult because of the roughened surfaces. For a conclusive evaluation of stability, the weight loss of Ni and Ti electrodes was measured after an extended period (60 h) of potentiostatic experiment as displayed in Table 1.



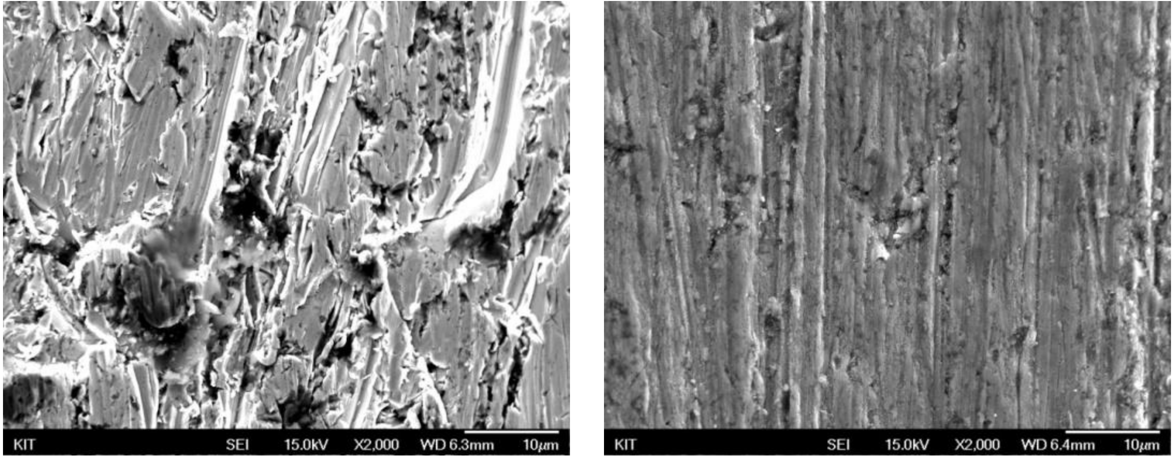
(a) Ni before the experiment

(b) Ti before the experiment



(c) Ni after the experiment in the KOH electrolyte

(d) Ti after the experiment in the KOH electrolyte



(e) Ni after the experiment in the BMIM·BF_4 electrolyte

(f) Ti after the experiment in the BMIM·BF_4 electrolyte

Figure 6. Changes in surface morphology of Ni and Ti electrodes before and after potentiostatic experiments (at -1.7 V for 30 min) in BMIM·BF_4 (12 wt%) and KOH (6 wt%) aqueous electrolytes (refer to the corresponding label to each picture and the magnification factor is 2000 for all cases).

Although Ti appears to have practically negligible weight loss in the KOH aqueous electrolyte, the corrosion of Ti is severe in the presence of BMIM·BF_4 in aqueous solution.

Firstly, the surface roughening of both electrodes can be explained by considering HF that could result from the aforementioned hydrolytic instability of BF_4^--containing ionic liquids as, in particular, Huang et al. reported the enhanced surface roughness of NiTi alloy in HF aqueous solution [22]. Secondly, the enhanced susceptibility of Ti to corrosion compared to Ni in the BMIM·BF_4 aqueous electrolyte can be attributed to the dissolution of Ti oxide layer, which otherwise becomes a protection layer, in the presence of HF [23,24]. It might be concluded that small pores are generated only on the surface of Ti in the presence of the ionic liquid with considering the substantial weight loss of Ti, which can be supported by Jakubowicz's paper where micropore formation on Ti surface was reported with HF addition [24]. Incidentally, the relatively better corrosion resistance of Ni to HF can be understood in the same context as Kirtzer et al.'s where the corrosion of Ni was negligible in a solution of HF [25].

Table 1. Weight loss of Ni and Ti electrodes after potentiostatic experiment (at -1.7 V for 60 h).

Electrolyte	**BMIM·BF_4 (12wt%)**		**KOH (6wt%)**	
Electrode	Ti	Ni	Ti	Ni
Weight loss (g)	0.2142	0.002	0.0006	0
Weight loss (mg/cm^2)	90.96	0.85	0.26	0

4. CONCLUSIONS

The reductive currents of Ni and Ti at low potentials in BMIM·BF_4 (12 wt%) and KOH (6 wt%) aqueous electrolytes should result from hydrogen evolution reaction with considering the electrolyte composition and the electrochemical window of the ionic liquid, which was confirmed by Pt electrode.

However, the different pH's of the electrolytes make the direct comparison of hydrogen evolution overpotential of an electrode difficult in the different electrolytes. While Ni and Ti have a more or less similar hydrogen evolution catalytic activity in alkaline electrolyte, the catalytic activity for hydrogen evolution at Ni is superior to Ti in the presence of BMIM·BF_4 in aqueous electrolyte. The existence of the ionic liquid in aqueous electrolyte appears to change the hydrogen evolution kinetics at both Ni and Ti electrodes as seen in the Tafel analysis. This is partly because BMIM·BF_4 is susceptible to hydrolytic decomposition of $BMIM^+$ owing to the hydrogen at C2 position and of BF_4^- incurring HF formation. The measurement of electrode weight loss after the potentiostatic experiment and the according SEM analysis show that the surfaces of Ni and Ti electrodes become roughened and small pores are generated only on the surface of Ti in the presence of BMIM·BF_4. This change in surface morphology is also attributed to HF that could be formed from the hydrolytic instability of BF_4^--containing ionic liquids.

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