



Comparative study of corrosion behavior of metals in protic and aprotic ionic liquids



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ABSTRACT

A comparative study of metal corrosion in a protic ionic liquid (PIL) and an aprotic ionic liquid (AIL) with the same anion is reported in this paper. The stability of Ni, Cu, Al, Zn, and Mg in 1-butylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BPyrr] [NTf₂]) PIL and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMPyrr] [NTf₂]) AIL is evaluated, and the measured corrosion potential (E_{corr}) and corrosion current density (i_{corr}) of these metals in both ionic liquids are compared. Electrochemical tests show that the PIL has a narrower electrochemical stability window and is generally more reactive toward the metals than the AIL. Even though the observed corrosion behavior is more or less similar in both ionic liquids, the corrosion parameters obtained reflect the fact that the presence of a proton on the cation of an ionic liquid makes metals more susceptible to corrosion, i.e. produces a lower E_{corr} and higher i_{corr} .

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1. Introduction

Ionic liquids are salts consisting of a large asymmetric cation and a complex anion, which are stable in the liquid phase below 100 °C [1]. Due to their useful properties, which include non-volatility, high conductivity and high electrochemical stability, ionic liquids are being used in an ever-increasing range of applications. In addition, ionic liquids can be tailored to specific tasks because their properties can be modified by changing the cation or the anion. Depending on the presence of an available proton on the cation, ionic liquids can be categorized as either protic or aprotic [2]. Protic ionic liquids (PILs) are easier to synthesize than aprotic ionic liquids (AILs) via a simple atom-economic neutralization reaction that involves the transfer of a proton from a Bronsted acid to a Bronsted base [3]. Although PILs have narrower electrochemical stability windows than AILs [4], the proton availability in PILs is a crucial factor in many applications. In the electrochemistry field, PILs can be used as electrolytes in fuel cells [5–7], in batteries [8–10] and supercapacitors [11,12].

Pyrrolidinium-based PILs have been claimed as superior conductors in which diffusion through a hydrogen bond network is the predominant proton transport mechanism (the Grotthuss mechanism) [3]. Meanwhile, a comparative study between PILs and AILs with identical anions reported by Vogl et al. [13] confirmed that 1-butylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BPyrr] [NTf₂]) PIL showed

comparable conductivity and viscosity to 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMPyrr] [NTf₂]) AIL. Interestingly, electrodes in [BPyrr] [NTf₂] showed a higher discharge capacity than those in [BMPyrr] [NTf₂] during charge-discharge tests in the presence of lithium salt [13]. Due to the promising electrochemical performance of PILs and the fact that their synthesis is more economical than that of AILs, the use of PILs in electrochemical devices continues to increase.

Another important aspect that must be addressed in practical applications of ionic liquids is the stability or compatibility of the materials with which they come into contact. The interaction of ionic liquids with engineering materials is one of the key points in determining the viability of a system to be implemented on an industrial scale [14]. To our knowledge, there are currently no data on the stability of metallic materials in PILs. In this study, the corrosion of some metals commonly used in electrochemical devices (Ni, Cu, Al, Zn and Mg) is studied in [BPyrr] [NTf₂] PIL and compared with their corrosion in [BMPyrr] [NTf₂] AIL. The corrosion parameters of the metals in both ionic liquids are evaluated; these could help in selecting materials for use in different ionic liquid systems.

2. Material and methods

[BPyrr] [NTf₂] PIL and [BMPyrr] [NTf₂] AIL (water content ~90 ppm) used in this study were purchased from C-TRI Korea and were dried in a vacuum oven at 100 °C for 24 h before use (water content after drying ~20 ppm). Schematic structures of both ionic liquids are displayed in Fig. 1. Electrochemical measurements were conducted in a three-

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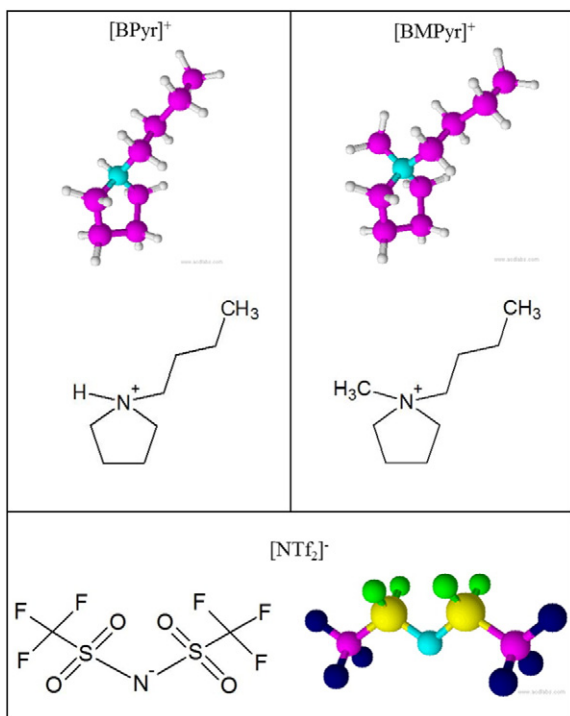


Fig. 1. Schematic structures of protic [BPyr]⁺ cation, aprotic [BMPyr]⁺ cation, and [NTf₂]⁻ anion.

electrode system with metal foil (metal = Ni, Cu, Al, Zn, and Mg) as a working electrode, and Pt wire (0.5 mm in diameter) and coiled Pt wire (0.25 mm in diameter) as a quasi-reference and a counter electrode, respectively. All potentials are reported versus ferrocene/ferrocenium (Fc/Fc⁺) redox couple. The exposed surface areas of the working electrodes were 0.265 cm² for Al and Zn, and 0.254 cm² for Ni, Cu and Mg. The electrodes were polished with a 1500 grid SiC paper, and the working electrodes were further polished with 0.05 μm alumina on an alumina polishing pad. The polished electrodes were cleaned with distilled water and acetone, and then dried prior to use. Cyclic voltammetry was performed using a WPG 100 (WonATech) potentiostat at a scan rate of 10 mV/s, while potentiodynamic anodic polarization was performed using a Versastat3.0 potentiostat at a scan rate of 0.1667 mV/s from −0.5 V below open circuit potential (E_{OC}) to 3 V above E_{OC} . All measurements were conducted at room temperature. The corrosion current density (i_{corr}) was determined from the slope of the potential vs. current density plot within a potential range of ± 50 mV from E_{OC} .

3. Results and discussion

Cyclic voltammetry of neat [BPyr] [NTf₂] PIL and [BMPyr] [NTf₂] AIL was conducted on a gold electrode to compare the electrochemical stability windows of both ionic liquids, and the results are shown in Fig. 2. While there are no available literature data on the stability potential window of [BPyr] [NTf₂] PIL, the potential window of [BMPyr] [NTf₂] AIL obtained in this work agrees well with previous reports [15,16]. The PIL has a narrower window due to a more positive cathodic stability limit potential at −1.2 V, while the [BMPyr]⁺ cation of AIL shows stability up to −3.3 V. This phenomenon is in accordance with previous works reported in the literature, which showed that PILs containing the [BPyr]⁺ cation have an electrochemical stability window 2 V narrower than AILs with the same anion but containing the [BMPyr]⁺ cation [17,18]. The presence of a dissociatable proton in [BPyr]⁺ is expected to withdraw electrons more actively and reduce the cation at a

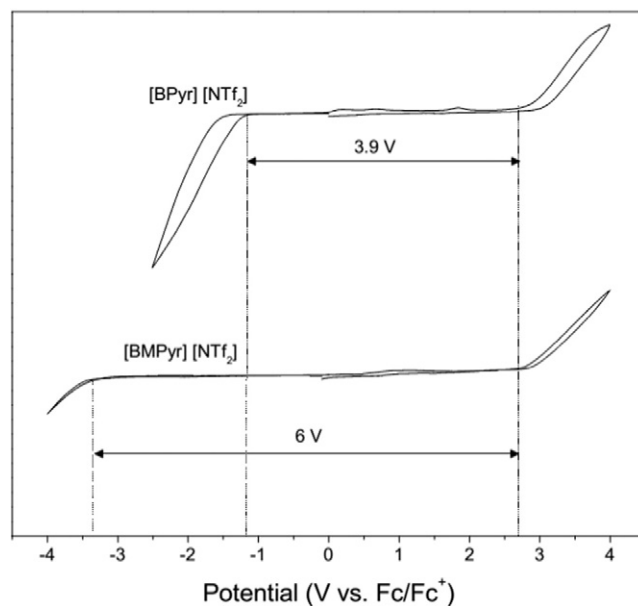


Fig. 2. Electrochemical stability window of [BPyr] [NTf₂] PIL and [BMPyr] [NTf₂] AIL on gold electrode.

more positive potential than the methyl functional group of [BMPyr]⁺ [2,4].

Fig. 3(a) and (b) show the anodic polarization of Ni, Cu, Al, Zn and Mg in [BPyr] [NTf₂] and [BMPyr] [NTf₂], respectively. In general, there is some similarity between the observed corrosion behaviors in the PIL and the AIL. Al shows a steady current increase above the corrosion potential (E_{corr}) and the slope becomes less steep at a potential above 0.7 V and 1.2 V in the PIL and the AIL, respectively. Zn and Mg suffer from rapid dissolution right above E_{corr} and immediately reach a steady current density in both ionic liquids. On the other hand, Cu in the PIL shows a narrow passive region from E_{corr} to 0.5 V and subsequent passive film breakdown, while active dissolution was observed at a few hundred millivolts above E_{corr} in the AIL. This phenomenon is noteworthy, considering that Cu is known to undergo active dissolution without passivation in other ionic liquids such as chloroaluminate- and dicyanamide-based ionic liquids [19–21]. Dissociated protons from the cation might participate in the passivation mechanism of Cu in PILs.

A linear polarization method was used to calculate i_{corr} in each system by plotting current density at a small potential range around E_{corr} . The slope ($\Delta E/\Delta i_{applied}$) is called the polarization resistance (R_p), and is inversely proportional to i_{corr} from the relation expressed in the equation below:

$$R_p = \frac{\Delta E}{\Delta i_{applied}} = \frac{\beta_a \beta_c}{2.3 i_{corr} (\beta_a + \beta_c)}$$

where β_a and β_c are the anodic and cathodic Tafel constants, respectively. To avoid ambiguity in the choice of Tafel region, β_a and β_c values were chosen to be 0.1 V/decade as this common choice can be justified with negligible error to an actual corrosion rate value [22]. The E_{corr} and i_{corr} values of all metals in both ionic liquids are shown in Fig. 4, which also gives the average values and error bars of E_{corr} and i_{corr} from linear polarization experiments carried out in triplicate. From the comparison of E_{corr} and i_{corr} , we can draw the general conclusion that replacement of the methyl functional group with a proton makes the metals more susceptible to corrosion in terms of lower E_{corr} and higher i_{corr} . More specifically, the E_{corr} values are lower in the PIL except for Mg, which shows a similar E_{corr} value in both ionic liquids. Mg and Al display definite enhancement in i_{corr} , whereas Cu, Ni and Zn have a similar level of i_{corr} within the margin of error. However, [NTf₂]-based ionic liquids are not highly corrosive and even the highest i_{corr} value of Mg is still much

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