



## Corrosion properties of metals in dicyanamide-based ionic liquids



Yi-Chen Wang<sup>a</sup>, Tai-Chou Lee<sup>a</sup>, Jheng-Yi Lin<sup>b</sup>, Jeng-Kuei Chang<sup>a,b,c,\*</sup>, Chuan-Ming Tseng<sup>d</sup>

<sup>a</sup> Department of Chemical and Materials Engineering, National Central University, Taoyuan, Taiwan

<sup>b</sup> Institute of Materials Science and Engineering, National Central University, Taoyuan, Taiwan

<sup>c</sup> Department of Mechanical Engineering, National Central University, Taoyuan, Taiwan

<sup>d</sup> Institute of Physics, Academia Sinica, Taipei, Taiwan

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### ABSTRACT

Corrosion behavior of metals in 1-ethyl-3-methylimidazolium–dicyanamide, butylmethylpyrrolidinium–dicyanamide, and 1-ethyl-3-methylimidazolium chloride–chloroaluminate ionic liquids (ILs) is studied. The constituent anions, rather than the cations, are the predominant species that govern the IL corrosivity toward materials. Among the materials investigated, Ni shows the lowest corrosion current and the best resistance against anodic dissolution in the three ILs. In the dicyanamide-based ILs, 304 stainless steel, Ti, and Al also exhibit satisfactory anti-corrosion characteristics. However, the use of Cu, carbon steel, and Mg in the same environment should be avoided due to their poor corrosion resistance, especially under anodic polarization conditions.

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### 1. Introduction

Ionic liquids (ILs), also called room-temperature molten salts, characterized by intrinsic ionic conductivity, wide electrochemical potential windows, good thermal stability, non-volatility, and non-flammability [1,2], have received increasing interest in both academic and industrial fields over the past decade. Since the physical and chemical properties of ILs can be designed by selecting appropriate cation/anion combinations [3], these task-specific liquids [4] have found a wide range of applications in purification, catalysis, analysis, separation, photoluminescence, electrochemistry, and energy-related applications [5–8]. Moreover, the “green” characteristics of ILs make them promising solvents in light of environmental concerns.

Utilization of ILs inevitably involves their storage, transportation, and operation, which cause various corrosion problems to the contact materials. In the ambient atmosphere and traditional aqueous solutions, corrosion-resistant metals rely on the formation of surface oxide layers (i.e., passive films) for protection against corrosion. However, ILs are non-aqueous liquids with low oxygen content but extremely high concentrations of cations and anions, and thus unfavorable environments for oxide film formation. The corrosion behavior and mechanism in ILs can be totally different from those in conventional environments; however, these issues have rarely been addressed. Uerdingen et al. investigated

material corrosion behavior in various flowing ILs under open-circuit conditions [9]; stainless steel (SS) proved to have the best resistance to erosion corrosion, while Cu generally showed high corrosion susceptibility. Perissi et al. studied the corrosion properties of metals in 1-butyl-3-methylimidazolium–bis-(trifluoromethanesulfonyl) imide (BMI-TFSI) at various temperatures and concluded that the corrosion rate (including that of Cu) at room temperature in this IL was low [10]. Tseng et al. [11] and Lin et al. [12] indicated that Ni and 304 SS have great corrosion resistance in a 1-ethyl-3-methylimidazolium chloride–chloroaluminate (EMIC–AlCl<sub>3</sub>) IL whereas Cu and Ti are severely corroded in the same environment. The nature of the constituent ions in ILs seems to play a role in IL corrosivity. However, the understanding of the mechanism of corrosion in ILs, although very critical, is rather limited. Further investigations are necessary.

ILs with dicyanamide anions (DCA<sup>−</sup>) are water-stable and air-stable electrolytes that have low viscosity and high conductivity [13–15]. Accordingly, DCA-based ILs have attracted a lot of attention in a variety of fields. For example, they can be used as reaction media for chemical syntheses and refining [16,17]. In addition, owing to their high solubility for metal salt precursors [18], they are ideal for electroplating various metals. Many active materials, such as Al, Mn, Ge, and Zn, were successfully electrodeposited in such ILs [19,20]. DCA-based ILs are also promising electrolytes for supercapacitors, allowing a high capacitance and high cell voltage [8]. Recently, secondary Li batteries incorporating a DCA-based IL electrolyte (a much cheaper alternative to TFSI-based ILs) was reported [21]. This kind of ILs has also been applied to solar cells, metal–air batteries, and electrochromic devices [22–24]. In the

\* Corresponding author. Address: National Central University, 300 Jhong-da Road, Taoyuan, Taiwan. Tel.: +886 3 4227151x34908; fax: +886 3 2805034.

E-mail address: [jkchang@ncu.edu.tw](mailto:jkchang@ncu.edu.tw) (J.-K. Chang).

above-mentioned applications, the ILs must be in contact with the pipes, processing equipment, containers, and other components in the energy-storage devices, leading to potential corrosion degradation. Accordingly, a detailed corrosion study of DCA-based ILs, which has never been performed, is the main task of this investigation.

In the present study, the corrosion properties of seven commonly used metals (Ni, Ti, Al, Cu, Mg, 304 SS, and carbon steel) were measured and compared in two types of DCA-based IL, namely 1-ethyl-3-methylimidazolium-dicyanamide (EMI–DCA) and butylmethylpyrrolidinium-dicyanamide (BMP–DCA). In addition, the material corrosion behavior in EMIC–AlCl<sub>3</sub> IL is examined for comparison. This is the first work that systematically studies how the constituent cations (EMI<sup>+</sup> and BMP<sup>+</sup>) and anions (DCA<sup>-</sup> and AlCl<sub>4</sub><sup>-</sup>) affect IL corrosivity toward various metals.

## 2. Experimental section

Seven common metals, namely Ni, Ti, Al, Cu, Mg, 304 SS, and carbon steel, were studied. The purities of Ni, Ti, Al, Cu, and Mg were above 99.9 wt.%. The carbon steel contained 0.13 wt.% C, 0.07 wt.% Si, 0.01 wt.% P, 0.013 wt.% S, and 0.73 wt.% Mn, and 304 SS contained 18.29 wt.% Cr, 8.17 wt.% Ni, 1.36 wt.% Mn, 0.02 wt.% C, 0.023 wt.% P, and 0.003 wt.% S. Each sample was connected to a Cu conductive wire and then mounted with epoxy resin, exposing a surface of 0.5 cm<sup>2</sup>. Before electrochemical testing, the samples were ground using successively finer abrasive papers to a grit of #4000. The corrosion properties of the electrodes were studied in EMI–DCA, BMP–DCA, and EMIC–AlCl<sub>3</sub> ILs at 25 ± 1 °C. For comparison, the corrosion behavior of the materials was also evaluated in 3.5 wt.% NaCl aqueous solution.

The DCA-based ILs were prepared and purified following a published method [18]. The ILs were washed with dichloromethane (99 wt.%, SHOWA), filtered to remove precipitates, and then vacuum-dried at 100 °C for 12 h before use. The EMIC–AlCl<sub>3</sub> IL was prepared by slowly adding anhydrous AlCl<sub>3</sub> powder into EMIC, which was synthesized as described in [25], until the AlCl<sub>3</sub> to EMIC molar ratio was 1:1 (becoming Lewis neutral) [26]. In this IL, EMI<sup>+</sup> and AlCl<sub>4</sub><sup>-</sup> are the main constituent species. The molecular structures of the ILs prepared are shown in Fig. 1. The water contents of the ILs, measured with a Karl Fisher titrator, were typically ~80 ppm by mass. All chemicals were handled and tested in an argon-filled glove box (Innovation Technology Co. Ltd.), where both the moisture and oxygen contents were maintained below 1 ppm.

A three-electrode electrochemical cell controlled by a potentiostat (AUTOLAB) was used for the corrosion tests. The sample was assembled as the working electrode. The reference electrode was a Pt wire placed in a fritted glass tube containing BMP–TFSI IL that had a ferrocene/ferrocenium couple (Fc/Fc<sup>+</sup> = 50/50 mol.%) as a potential standard. For preparation of the Fc/Fc<sup>+</sup> couple, 0.1 M of Fc

was first dissolved in BMP–TFSI IL. Then, a given anodic charge was applied to obtain 50 mol.% of Fc<sup>+</sup>. Two Pt wires were used for the electrolysis. Since the cathodic reaction during the Fc<sup>+</sup> synthesis is unclear, the cathode was placed in a separated tube, which has a porous grit to link the bulk electrolyte. This reference electrode showed a potential of +0.33 V vs. an Ag/AgCl electrode in 3 M KCl aqueous solution (equaled to +0.55 V vs. SHE). The counter electrode in the three-electrode testing cell was a Pt wire (with an exposed surface area of 1.25 cm<sup>2</sup>), which was directly immersed in the bulk IL (~10 mL). When the working electrode was a cathode (or anode) during the measurement, anodic (or cathodic) decomposition of IL anions (or cations) took place at the counter electrode [11]. The detailed reaction equations, however, are unknown. Although the ILs did not change color during the measurement, the decomposition products at the counter electrode may be introduced into the IL electrolytes and might affect the behavior of the working electrode.

After open-circuit potential (OCP) measurements for 10 min, potentiodynamic polarization tests of the electrodes were performed with a potential sweep rate of 5 mV/s (which is relatively fast for corrosion measurements) toward an anodic direction. The corrosion current density (*i*<sub>corr</sub>) was determined via extrapolation of the cathodic Tafel slope back to the corrosion potential (*E*<sub>corr</sub>). The Tafel slope was defined by a linear range, which is 200–500 mV below *E*<sub>corr</sub>, of the cathodic polarization curve. To investigate the material corrosion characteristics, the electrodes were held at the selected potentials for 1 h prior to the morphology examinations. After the potentiostatic etching, the samples were thoroughly cleaned with anhydrous alcohol and then dried in air. Their surface morphologies and chemical compositions were analyzed using a scanning electron microscope (SEM, Hitachi S-4700I) and its auxiliary energy-dispersive X-ray spectrometer (EDS), respectively.

## 3. Results and discussion

The thermodynamic activity of the metals in various environments was first evaluated by measuring the OCPs. Fig. 2 shows the data recorded in the three ILs and in the NaCl aqueous solution. As exhibited, all of the OCP values are quite stable, indicating that the electrode surface conditions approached equilibrium shortly after the electrodes were exposed to the solutions. In the EMI–DCA IL (Fig. 2(a)), the OCPs decrease in the sequence of carbon steel (−0.9V<sub>Fc/Fc<sup>+</sup></sub>) > Cu(−1.13V<sub>Fc/Fc<sup>+</sup></sub>) > Ni(−1.18V<sub>Fc/Fc<sup>+</sup></sub>) > 304SS(−1.25V<sub>Fc/Fc<sup>+</sup></sub>) > Ti(−1.5V<sub>Fc/Fc<sup>+</sup></sub>) > Al(−1.55V<sub>Fc/Fc<sup>+</sup></sub>) > Mg(−1.85V<sub>Fc/Fc<sup>+</sup></sub>), suggesting that carbon steel is the most noble while Mg is the most active in this environment. The same OCP order was found in BMP–DCA IL (Fig. 2(b)). Similar activity tendencies in the two DCA-based ILs were thus confirmed. Replacing the DCA<sup>-</sup> ions with AlCl<sub>4</sub><sup>-</sup> ions in the IL led to a clear change in the OCP sequence

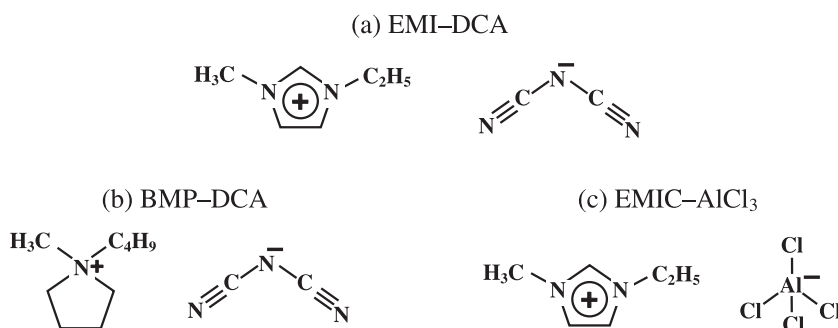


Fig. 1. Molecular structures of (a) EMI–DCA IL, (b) BMP–DCA IL, and (c) EMIC–AlCl<sub>3</sub> IL.

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