

## Anodic behavior of neodymium in acidic $\text{AlCl}_3$ -1-ethyl-3-methyl-imidazolium chloride ionic liquid

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**Abstract:** The anodic behavior of neodymium in acidic  $\text{AlCl}_3$ -1-ethyl-3-methyl-imidazolium chloride ( $\text{AlCl}_3$ -EMIC) ionic liquid was investigated by conducting linear sweep voltammeter and open potentialometry. The viscosity of Nd dissolved ionic liquid and the surface morphologies of Nd were characterized using an Ostwald viscometer and a scanning electron microscope, respectively. The chemical composition of Nd surface was identified by Raman spectra. The results showed that dissolution of Nd under anodic polarization occurred after the breakdown of oxide films. A viscous layer formed at the interface of Nd/ionic liquid during the galvanostatic process of 5 and 20 mA/cm<sup>2</sup>. The formation of viscous layer was attributed to the accumulation of Nd dissolved  $\text{AlCl}_3$ -EMIC ionic liquid, which had high viscosity. The oxide films could be removed thoroughly and the surface of Nd was homogeneous without etching pits, when viscous layer formed in the anodic process. Otherwise, the surface showed a pitting morphology.

**Keywords:** neodymium; ionic liquid;  $\text{AlCl}_3$ -1-ethyl-3-methyl-imidazolium chloride; anodic process; viscous layer; rare earths

The rare earth elements (REE) are a group of co-occurring metals (yttrium, the 15 elements in the lanthanide series, and sometimes scandium) with electronically special 4f structure and corresponding optical, magnetic, electrical and catalytic properties<sup>[1-3]</sup>. Because of their unique physical-chemical properties they were widely used in a growing number of applications and had become indispensable for a large variety of emerging technologies during the past three decades such as rare earth permanent magnets motors, magnetostrictive devices, ultrasonic transducer techniques, catalysts for automobiles, phosphors in lighting and computer, microwave absorbing materials, etc.<sup>[4-6]</sup>. However, due to the active chemical properties, rare earth metals are very vulnerable to oxidization and corrosion with the water and oxygen in the air which immensely limits the practical applications especially in the field of permanent magnets, magnetic refrigeration and magnetostrictive applications<sup>[7,8]</sup>.

Ionic liquids (ILs), also called room temperature molten salts, are comprised of solely ions, with melting temperatures below 100 °C. The ionic liquids have many excellent properties compared with conventional aqueous and organic solvents, such as intrinsic ionic conductivity, resistance to strongly oxidizing or reducing agents, good thermal stability, non-volatility, non-flammability, high stability against nuclear radiation and high selectivity<sup>[9-11]</sup>.

In recent decades, ionic liquids have been widely applied in electrochemical and other fields due to the useful solvent properties<sup>[12]</sup>. As a kind of excellent electrolyte, ionic liquids are attracting many researchers who are dealing with the study of electrochemistry concerning rare earth metals. In 2008, Legeai et al. reported that lanthanum (La) could be electrodeposited in ambient atmosphere in the ionic liquids containing anions such as tri-fluoromethyl-sulfonate<sup>[13]</sup>. At the same year, yttrium (Y), gadolinium (Gd) and ytterbium (Yb) were electrodeposited by Glukhov et al. in 1-butyl-1-methylpyrrolidinium triflate ionic liquid<sup>[14]</sup>. Lisenkov et al. reported that Al-Ce alloy coatings were electrodeposited in  $\text{AlCl}_3$ -1-butyl-3-methylimidazolium chloride ionic liquid doped with cerium chloride in 2010<sup>[15]</sup>. In 2012, compact neodymium (Nd) and dysprosium (Dy) electrodeposits with good adherence were obtained in triethyl-pentyl-phosphonium and bis(trifluoromethylsulfonyl)amide ionic liquid respectively<sup>[16,17]</sup>. Hussey et al. investigated the electrochemistry and absorption spectroscopy of Nd(III) and Pr(III) in the 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid with and without added  $\text{Cl}^-$  in 2014<sup>[18]</sup>. However, reports on the anodic behavior of rare earth metals in ionic liquids are still limited. Research on anodic behavior can provide guidelines for not only the research on electropolishing and electrochemical micromachining of rare earth metals

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in ionic liquids but also for the applications of soluble anodes in rare earth metals electrodeposition and electrorecycling. So fundamental studies on the anodic behavior of rare earth metals in the ionic liquids are highly demanded.

$\text{AlCl}_3$ -1-ethyl-3-methylimidazoliumchloride ( $\text{AlCl}_3$ -EMIC) ionic liquid is a sort of water-free electrolyte, which is a promising electrolyte for the electrochemical behavior research on water-sensitive metals<sup>[19,20]</sup>. The preparation of anti-corrosion coatings on rare earth alloys by electrodeposition in  $\text{AlCl}_3$ -EMIC ionic liquid was carried out by our earlier research. Al coatings were electrodeposited on La-Ce alloy from  $\text{AlCl}_3$ -EMIC ionic liquid at room temperature with excellent adhesion strength<sup>[21]</sup>. A dense, continuous and adhesive amorphous Al-Mn alloy layer was electrodeposited on NdFeB in  $\text{AlCl}_3$ -EMIC- $\text{MnCl}_2$  ionic liquid at room temperature<sup>[20,22]</sup>. Xu et al. first reported the formation of viscous layer during the anodic electrolytic etching process of NdFeB magnets in  $\text{AlCl}_3$ -EMIC ionic liquid which contributed to the complete removal of oxide films on the surface of the NdFeB<sup>[23]</sup>.

For the purpose of initial exploration of the anodic behavior of the rare earth metals in ionic liquid, as well as the further understanding of the formation mechanism of the viscous layer in the anodic electrolytic etching process of NdFeB magnets, the anodic behavior of Nd was carried out in  $\text{AlCl}_3$ -EMIC ionic liquid in this paper.

## 1 Experimental

Plates of Nd (purity 99.5% obtained from General Research Institute for Nonferrous Metals) were used in the experiments. Prior to the electrochemical process, the Nd plates were polished with abrasive papers up to grit 1000 and then ultrasonically cleaned with acetone. The apparent area of the Nd plates for study was  $1\text{ cm} \times 1\text{ cm}$  by sealing the other portion with an adhesive band. The acidic  $\text{AlCl}_3$ -EMIC ionic liquid was prepared by slow addition of anhydrous  $\text{AlCl}_3$  powder (99.99%, Alfa Aesar) into the EMIC in a beaker at room temperature until the molar ratio of  $\text{AlCl}_3$  to EMIC was 2:1. The mixture was continuously stirred by a magnetic bar for one day, and then refined with pure Al wires for one week in order to remove the impurities. The water content of the dried ionic liquid was measured to be 800 ppm by Karl-Fischer titration. All the experiments were performed in an argon-filled glove-box at room temperature (25 °C), in which the oxygen content and moisture were maintained below 1 ppm.

A three-electrode cell connected to a Princeton Applied Research Parstat 2273 potentiostat/galvanostat was used for the measurements of open circuit potential (OCP), linear sweep voltammetry and galvanostatic polarization. The Nd plate was set as a working electrode,

with the pure Al plate (99.999%) as a counter electrode and the pure Pt wire as a quasi-reference electrode. The linear sweep voltammetry was performed from OCP to 1000 mV with sweep rates of 1, 5 and 10 mV/s respectively. The current densities for galvanostatic polarization were 2, 5 and 20  $\text{mA}/\text{cm}^2$  respectively.

A two-electrode cell was used for the anodic dissolution (with a magnetic bar continuously stirring). The Nd plate was assembled as a working electrode and the Al plate as a counter electrode. The current density was set as 20  $\text{mA}/\text{cm}^2$ . The viscosity of the Nd dissolved ionic liquid was measured using an Ostwald viscometer at 25 °C and the mass loss of Nd was measured by a microbalance.

A field emission gun scanning electron microscope (FEG-SEM) was used to characterize the surface morphologies of Nd plates. The surface chemical composition of samples was identified by means of an energy dispersive X-ray spectroscope (EDS) coupled to the SEM instrument. Raman spectra measurements were performed on a Raman microscope with the detector of Pixis-100BR CCD (Princeton Instrument), the dispersion system of Acton SP-2500i spectrograph and the excitation source of a 20 mW He-Ne laser (632.8 nm).

## 2 Results

### 2.1 OCP behavior of Nd

Fig. 1 depicts the potential variations of Nd towards time without current flow through the electrode. Curve (1) shows the OCP results of Nd electrode experienced additional exposure time (900 s) to the air before measurements. The potential starts at about -400 mV, and then rapidly drops in the negative direction until it reaches -1000 mV. This process covers a time interval of approximately 400 s. Thereafter, the potential scatters between -940 mV and -1000 mV without plateau. For the sample transferred into the glove-box immediately after pretreatment (0 s), the result is shown in Curve (2).

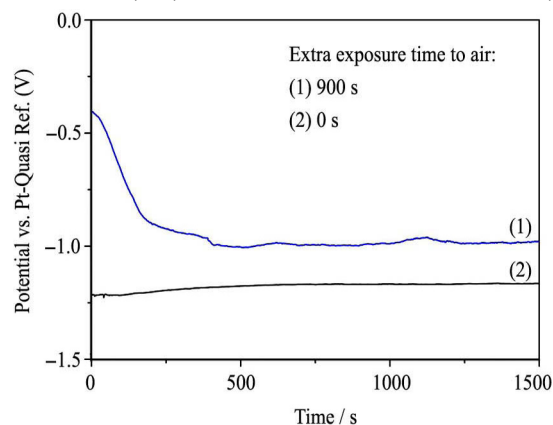


Fig. 1 Variation of potential with time for Nd

(1) Exposed to the air for additional 900 s before measurement;  
(2) Measured immediately after pretreatment

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