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Exchange Current Density of Gd(III)/Gd Reaction in LiCl-KCl Eutectic and Analysis of Errors Caused by Various Methods

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ABSTRACT

Reliable measurement of exchange current density i_0 is important for systems using molten salts as electrolyte or/and coolant. The values of i_0 of Gd(III)/Gd reaction in LiCl-KCl eutectic at different $GdCl_3$ concentrations (1 – 9 wt%) and temperatures (723 – 823 K) are reported. The values are determined by optimization fitting method using the non-simplified electrode kinetics equation, and other three commonly used methods including Tafel method, linear polarization (LP) method, and electrochemical impedance spectroscopy (EIS) method. Results show that significant errors can be introduced by using the three conventional methods in the mass-transfer involved case as they are based on the simplified electrode kinetics equations with an assumption of no mass-transfer effect. The optimization fitting method shows more reliable results but has limitations at 1 wt% Gd concentration. The standard rate constant k^0 values determined by the optimization fitting are 4.93 – 9.22 × 10^{-5} cm/s in the studied temperature range and the activation energy is 31.0 kJ/mol.

Key words: Exchange current density; Molten salts; Gadolinium; Pyroprocessing; Rare earth.

1. Introduction

Using of molten salt electrolytes has many advantages over aqueous and organic electrolytes in many applications [1]. Some examples are fuel cell [2], molten salt battery [3], separations and recovery of critical rare earth materials [4], nuclear fuel processing and used fuel recycling [5]. One of the main advantages of its using as electrolyte is the faster electrode reaction rate [1]. Exchange current density for an electrode couple is the key parameter that defines the reaction rate on the electrode surface. There are many recent studies on the determining of i_0 for hydrogen production on the electrode for molten salt fuel cell and reduction reactions of actinides and fission products for pyroprocessing of the used nuclear fuel (UNF) [2,6-12]. Due to the high operating temperature and excellent thermal properties, molten salts have also been proposed for use as heat transfer and storage fluids in many energy conversion systems such as molten salt nuclear reactors (MSR) [13] and concentrating solar power applications (CSP) [14]. The drawback of using molten salt as electrolyte and coolant is the accelerated corrosion of materials at high temperature [1,13-15]. Evaluation and simulation of materials performance in these applications are critical for safe operation and requires the measurement of kinetic parameter i_0 for the material dissolution [16].

We have noticed that many recent studies investigated the exchange current density of U(III)/U [6-8], Th(IV)/Th [9,10], Ce(III)/Ce [11,12], Gd(III)/Gd [13], and Mg(II)/Mg [8] in molten salts using Tafel method, LP method, and electrochemical impedance spectroscopy (EIS) method. These methods are convenient and widely used in aqueous solution. However, electrode reaction is faster in molten salt than that in aqueous solution, and the reaction rate on the electrode surface could be limited by the mass transfer rate of reactants from the bulk solution to the electrode surface. Significant errors of i_0 determined by Tafel, LP, and EIS method are possible as these methods are based on the simplified kinetics equation with an assumption of no mass-transfer effect.