

Fluoride addition effect on the EXAFS of neodymium cation in molten chlorides

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Introduction

Neodymium magnet has the strongest magnetism among the magnets currently industrialized, thus it has been used as motors in hybrid cars, electric vehicles, wind farms and medical instruments which are required with strong magnetism. However, over 97 % of the first resource of rare earths including neodymium is now produced in China. If the demand of the electric vehicles and wind farms rapidly increases in the world, it leads to special concern about the lacking of rare earth resource. Therefore, we have focused on nickel misch metal hydride batteries as a secondary resource of rare earths, and investigated applicability of molten salt electrolysis to extract neodymium from them. To find out the much efficient electrochemical condition for the separation of neodymium, the electrochemical behaviour of neodymium in molten LiCl – KCl and LiCl – CaCl₂ eutectic coexisting various amount of LiF has been examined. To elucidate the relationship between the variation of electro-reduction potential and local structure around neodymium cation depending on fluoride concentration in molten chloride, EXAFS experiments of neodymium cation in molten LiCl – KCl – LiF and LiCl – CaCl₂ – LiF have been performed.

Experimental

EXAFS spectra of Nd L_{III}-edge (6.209 keV) were collected with a fixed time scan method by using Si (111) double crystal monochromator in transmission mode. Mixtures of NdCl₃ (*x* = 5mol%) in eutectic LiCl – KCl or LiCl – CaCl₂ with LiF in the amount of various times to the concentration of NdCl₃ (0 to 10), were melted once in a glassy carbon crucible at 873 K in a glove box filled with an argon atmosphere in high purity. Then, they were mixed with boron nitride powder, and pressed into pellets. To prevent from the chemical reaction during heating process in EXAFS measurements, these pellets were installed in a cell made with pyrolytic boron nitride and the electric furnace was filled with He gas under 30 kPa. EXAFS data were analysed by using the WinXAS ver.3.1.

Results and discussion

The structural functions of molten NdCl₃ – LiCl – KCl – LiF (0 and 6 times of concentration of Nd) and NdCl₃ – LiCl – CaCl₂ – LiF (0, 6 and 10 times of concentration of Nd) at 873 K are shown in Fig. 1. In both systems, with increasing fluoride concentration, interionic distance between Nd³⁺ and anion decreases, that is corresponding

to the fact that chloride anions in the 1st coordinated sphere around Nd³⁺ are exchanged by fluoride anions. The most striking feature derived from these figures is the local structure of Nd³⁺ is more affected by fluoride addition in LiCl – KCl eutectic than in LiCl – CaCl₂ eutectic. This is due to the difference of coulombic interaction, i.e., Ca²⁺ much strongly coordinates F⁻ than K⁺ does, thus it prevents fluoride coordination around Nd³⁺ in the first coordination sphere. It has been found that the tendency of the variation of electro-deposition potential depending on fluoride concentration is different, thus profound discussion on the relationship between electrochemical behaviour and local structure is now expected.

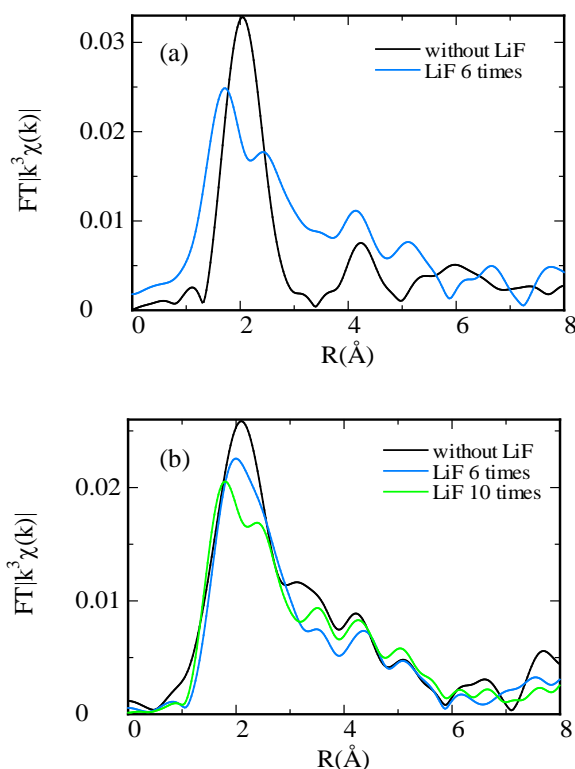


Fig. 1 The structural functions of molten (a) NdCl₃ – LiCl – KCl – LiF (0 and 6 times of concentration of Nd) and (b) NdCl₃ – LiCl – CaCl₂ – LiF (0, 6 and 10 times of concentration of Nd) at 873 K.

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