Supplementary Information

A New Approach for the Preparation of Variable Valent Rare Earth Alloys from Nano Rare Earth Oxide at Low Temperature in Molten Salt

Milin Zhang,^{*a*} * Yongde Yan,^{*a,b**} Wei Han,^{*a*} Xing Li,^{*a*} Zhiyao Hou,^{*a*} Yang Tian,^{*a*} Ke Ye,^{*a*} Lihong Bao,^{*c*} Xiaodong Li,^{*c*} and Zhijian Zhang^{*b*}

^aKey Laboratory of Superlight Materials and Surface Technology, Ministry of Education, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

E-mail: zhangmilin@hrbeu.edu.cn, y5d2006@hrbeu.edu.cn

Fax: +86 (0)451 82533026; Tel: +86 (0)451 82533026

^bCollege of Nuclear Science and Technology, Harbin Engineering University, Harbin 150001, China

^cDepartment of Mechanical Engineering, University of South Carolina, 300 Main Street, Columbia, South Carolina 29208, USA

Supplementary Fig. 1 shows the CVs obtained on molybdenum electrodes (S =0.322cm²) at various scan rates and cathodic limits with the addition of 2 wt. % AlCl₃ and 1wt. % nano-Sm₂O₃, nano-Yb₂O₃, and nano-Eu₂O₃ in LiCl-KCl melts at 480 °C, respectively. The peak currents increase with the increase of scan rate. From Fig. 1a, since the deposition of Al is close to the reduction one of the Sm(III) to Sm(II), the reducation/oxidation peaks (E1/E1') prior to Al redox couple (A/A') could be related to the redox reaction of Sm(III)/Sm(II) or the formation and oxidation of Al-Mo alloy, or their combination. In order to figure out who is responsible for the peaks E_1/E_1' . We carried out the CVs obtained on molybdenum electrodes at various scan rates in KCl-LiCl-AlCl₃-Yb₂O₃ melts (see Fig. 1b), due to a larger potential difference between deposition potential of Al and reduction one of the Yb(III) to Yb(II). The redox peaks (E_2/E_2') occurring at about -0.5 V correspond to the reduction/oxidation of Yb(III)/Yb(II). The shoulder F' prior to Al oxidation peak is likely to be associated with the oxidation Al-Mo alloy deposited. To further investigate the formation of Al-Mo alloy, the CVs at various scan rates in KCl-LiCl-AlCl₃-Eu₂O₃ melts with a narrow potential window were performed (see Fig. 1c). One couple of redox current waves prior to Al redox peaks truly exists. Sometimes its cathodic current is easy to be hidden by a larger-scaled cathodic current of Al reduction and it is hard to be wider discovered. Oppositely, а CV with a potential window in KCl-LiCl-AlCl₃-Eu₂O₃ melts was conducted (Fig. 1d). The cathodic and anodic limits of the electrochemical window correspond to the reduction of Li⁺ and the oxidation of chloride ions, respectively. The redox peaks (E_3/E_3') occurring at about 0 V correspond to the reduction/oxidation of Eu(III)/Eu(II). No formation or oxidation current of Al-Mo alloy is observed in the potential range of +1.0 to -1.5 V. We interpreted that as due to the small formation current of Al-Mo alloy. The discussion of Al-Mo alloy formation peaks can be available as supplementary information.







Supplementary Fig. 1 CVs obtained on molybdenum electrodes (S = 0.322cm²) at various scan rates and cathodic limits with the addition of 2 wt. % AlCl₃ and 1wt. % (a) nano-Sm₂O₃ (b) nano-Yb₂O₃ (c,d) nano-Eu₂O₃ in LiCl-KCl melts at 480 °C.