

Corrosion Control of Er_2O_3 in Li as Insulating Material for Liquid Li Blanket System

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Abstract. Electrically insulating coating to mitigate MHD pressure drop in liquid Li blanket system is underdevelopment and Er_2O_3 is regarded as leading candidate material. Recent studies have showed Er_2O_3 can be corroded reacting O in Li and control of O in Li blanket system was necessary. In this study, LiErO_2 was newly synthesized to measure electrical resistivity to estimate degradation of Er_2O_3 coating by corrosion. Measurement result suggests electrical resistivity of LiErO_2 is low and it will be a critical problem. Next, Immersion test of Er in Li was carried out and it suggest removal of initial metal impurities is important for liquid Li blanket system.

1. Introduction

Blanket is one of the key components for magnetic confinement fusion reactor to achieve sustainable tritium cycle and economically efficient fusion energy. Liquid Li is attractive liquid tritium breeder for DEMO reactor for its low density, high tritium breeding ration without neutron multiplier, low melting point and low tritium leakage. These characteristics lead to compact and highly efficient self-cooled blanket system. One of the major issues for Li blanket system development is magneto-hydrodynamic (MHD) pressure drop caused from strong magnetic field applied from SC magnet in the reactor[1]. The MHD pressure drop can be mitigated by fabricating electrically insulating coating to decouple Li and structural material[2]. Corrosion tests of insulating materials in high temperature liquid Li were carried out[3] and Er_2O_3 became promising candidate material for its chemical stability in Li. Many coating methods are under development. Physical vapor deposition methods such as RF plasma sputtering deposition or arc plasma depositions were developed[4]. Crystallinity, orientation and adhesion of these coatings depended on deposition temperature or annealing process after deposition. In-situ coating were developed to fabricate coating in Li[5]. Self healing coating is also performed by doping O into V alloy[6]. Recent focused are on multilayer coating to prevent electrical leakage due to cracks, chemical corrosion or erosion on Er_2O_3 layer[7]. Although Er_2O_3 regarded as leading insulating material for MHD coating, detailed chemical behavior in liquid Li were not clear. Authors' recent researches have showed Er_2O_3 forms LiErO_2 as corrosion product in high temperature Li[8]. It is also found reaction rate to form LiErO_2 depends on O concentration in Li and higher O concentration makes higher corrosion rate[9]. Properties of LiErO_2 are still not clear and it is necessary to investigate how production of LiErO_2 affects the insulating properties of Er_2O_3 coating.

In this study, synthesis of LiErO_2 was tested in two methods, solid state sintering method and liquid Li synthesis method. Better LiErO_2 was synthesized by latter methods and primary measurement of electrical resistivity was carried out. Next, immersion of Er into Li is performed to investigate sensitivity of Er and Er_2O_3 to impurities. These studies showed electrical resistivity of LiErO_2 was more than 10^3 lower than Er_2O_3 and other insulating materials. These materials are sensitive for initial non-metal impurities and O control system in Li blanket system is necessary

2. Synthesis and Electrical Resistivity of LiErO₂

Synthesis test of LiErO₂ was tried by two methods, solid state sintering and liquid Li synthesis.

2.1. Solid state reaction

Ternary oxide includes Li, such as Li₂TiO₃ or LiAlO₂, can be sintered from Li₂O₃ and metal oxide. For LiErO₂ the reaction was assumed as below



In this study, powder of Li₂CO₃ and Er₂O₃ were used as starting material, and these reagents had more than 99.9% purity. These powders were mixed with 1:1 mole ratio and milled by a planetary ball mill for 30 min. Next, the mixed powder was pressed into a 10 mm rectangular pellet with 1mm thickness. The shaped pellet were heated in an electrical furnace in air atmosphere. This heating was up to 1273 K and treatment time was up to 24 hours. Heating rate and cooling rate was about 8 K/min. After this sintering, pellet was analyzed with XRD.

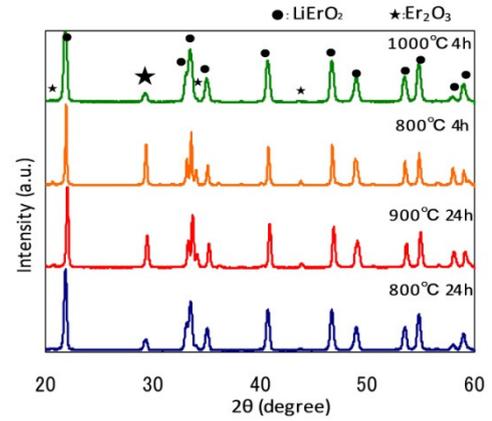
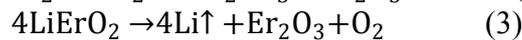
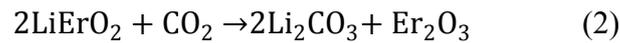


FIG.1. XRD spectrums of LiErO₂ synthesized by solid state reaction

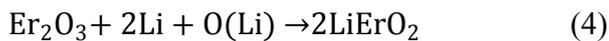
XRD spectrums of some specimens are shown in FIG.1. All specimens have Er₂O₃ and LiErO₂ peaks.

Detection of peaks of Er₂O₃ means remaining of Er₂O₃ and impurity of LiErO₂. Detection of Er₂O₃ may come from several reasons, such as non-reacted material remaining, evaporation of Li and absorption of CO₂. If sintering time was too short or shaped pellet was not uniform, non-reacted material remain. Saturated vapor pressure of Li is high in high temperature like 800^oC and it makes Li evaporation. These reactions can be written as follows,



2.2. Synthesis in liquid Li

From authors' previous researches, Er₂O₃ forms LiErO₂ in high temperature liquid Li and higher O concentration make higher reaction rate. Therefore, it is possible to synthesize LiErO₂ in Li from Er₂O₃ and O. The reaction is considered as below.



To make this reaction, 5g of Er₂O₃ powder, 3g of Li₂O powder and 12 g of liquid Li were introduced into stainless steel capsule. This capsule was packed by metal seal under Ar atmosphere. The capsule was kept at 973 K for 250 hours to precede the reaction. After this duration,

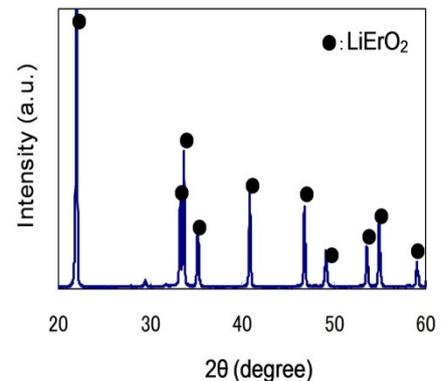


FIG.2. XRD spectrums of LiErO₂ synthesized in liquid Li

the capsule was open and Li was removed by water. Remaining powder was analyzed by XRD.

XRD spectrum of this powder is shown in FIG.2. The peak pattern is almost same with that of LiErO_2 . However, there are small addition peak around 29° . Although this is not perfectly pure LiErO_2 , the purity is better than that synthesized by solid state reaction. Moreover, the properties of this LiErO_2 will be more similar to the corrosion product which forms on Er_2O_3 coating during the Li blanket operation. Therefore, this LiErO_2 was used for electrical resistivity measurement.

2.3. Electrical resistivity measurement of LiErO_2

The powder of LiErO_2 was sintered to make LiErO_2 pellet for electrical resistivity measurement. Sintering needs low temperature and vacuum atmosphere, because LiErO_2 may change its state by heating, Li evaporation and CO_2 absorption. 0.5 g of LiErO_2 powder was sintered by Sparked Plasma Sintering (SPS) method to be shaped to pellet with 10 mm diameter. The treatment was in vacuum of 8 Pa, and press pressure was 5.6kN. The heating rate was 50K/min and cooling rate was 20K/min. The sintering temperature was from 473 K to 573 K and the sintering time was 1 min. The electrical resistivity of LiErO_2 was measured with the set up shown in FIG.3. A center electrode and a guard electrode were made on front side of the specimen. This guard electrode was for prevention of leakage current through the side surface. The center electrode was made by an electrically conductive tape, and the guard electrode was made by Ag paste. On the other side, the counter electrode was made by Ag paste. The electrical resistance was measured by KEITHLEY 6512 electrometer in air.

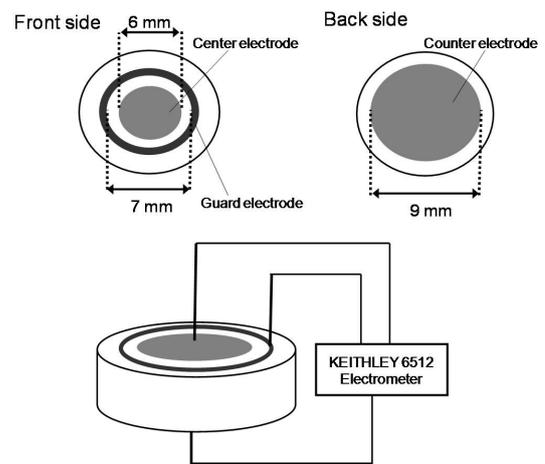


FIG.3. Set up of electrical resistivity measurement of LiErO_2

Measured electrical resistivity of LiErO_2 was 1.9×10^8 Ohm cm. It is 3 order lower than that of Er_2O_3 which was measured as 2.4×10^{11} Ohm cm, using same equipments. Also comparing with previous researches[10], electrical resistivity of LiErO_2 seems lower than other insulating materials. This research's measurement is at room temperature and under air atmosphere. Also purity of LiErO_2 was not confirmed. Therefore, more accurate measurement is necessary to estimate accurate electrical resistivity drop of practical condition. However, the measurement suggest corrosion of Er_2O_3 seems to be critical problem and O controlling system to prevent LiErO_2 formation is necessary for Li blanket system.

3. Sensitivity of Corrosion to O concentration

Er plate was immersed into Li using stainless steel pod. Inside the pod, Mo crucible was capsule. Immersion time was 50 h and immersion temperature was 973K. Pure Ar or 100 ppm O gas was flown by 50 cc/min. Specimen was extracted from Li after immersion and cleaned with water.

XRD spectrum of specimen immersed under 100ppm O flow is shown in FIG.4. There are peaks of Er, Er₂O₃ and ErN. The ErN may come from N impurity in Li. Also, spectrum of Er₂O₃ immersed using stainless steel capsule was shown in same figure. There are LiErO₂ peaks even there is no additional O. O for this corrosion came from initial impurities of Li and initial surface of crucible or capsule. These results shows Er₂O₃ and Er are sensitive for initial impurities such as O or N. Er was used as O getter for previous study and it may contaminated by N. Also Y is considered as T getter for Li blanket system and contamination by O and N can be recognized as large issue. Therefore, O and N purification before operation of Li blanket system using these materials are critical.

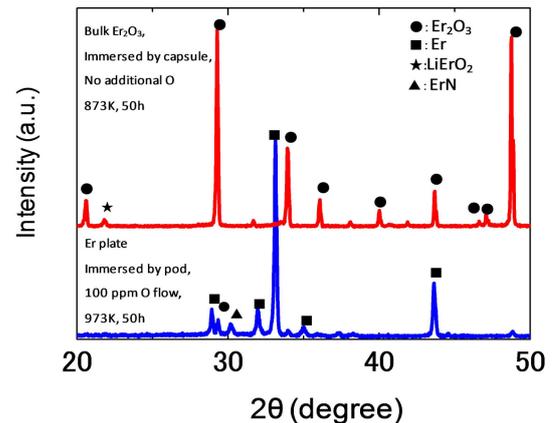


FIG.4. XRD spectrums of Er and Er₂O₃ immersed in Li

4. Conclusions

Synthesizing and electrical resistivity measurement of LiErO₂ was carried out. Relatively pure LiErO₂ can be synthesized by using liquid Li synthesizing method. The electrical resistivity of LiErO₂ was critically low compared to other insulating materials and O control to prevent LiErO₂ formation is necessary.

Immersion tests of Er and Er₂O₃ shows reactions with O and N are fast and significant even with impurity O and N. Treatment of these non-metal impurities before Li blanket operation are important.

Acknowledgement

This work was supported by Grand-in-Aid for JSPS Fellows.

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