Fundamental analysis for electrochemical removal and monitoring of oxide impurities in lead lithium using LiCl-KCl melt

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ABSTRACT

The electrochemical treatment using chloride molten salt was focused as a method for removal and monitoring of oxide impurities in the liquid breeder materials. The anodic reactions on a glassy carbon electrode in a LiCl-KCl eutectic melt contacting with Li-Pb eutectic melt without and with Li_2O addition were investigated. The transfer of oxide impurities to the molten salt from liquid metal was proved by the change of the concentration of oxide ions in the molten salt estimated from the cyclic voltammetry. The content of oxide impurities in the Li-Pb can be estimated by calculating backward from the transfer ratio and this technique may also be applied to monitoring. The visual observation and the weight loss of the anode indicated that the oxide impurities transferred to the molten salt could be removed as gases such as CO_2 by applying a voltage between an anodic glassy carbon rod in the molten salt and the Li-Pb used as a cathode.

1. Introduction

The liquid Li-Pb eutectic alloy (described below simply as Li-Pb) is expected to be used in the liquid blanket system in a fusion reactor [1–3]. The water-cooled lithium-lead breeding blanket is one of the candidate systems considered for the implementation in the European Demonstration Power Plant (DEMO) nuclear fusion reactor [3]. This functional material is thought to be easy to contain light impurities such as oxygen so that a removal and monitoring method for these impurities are important however they have not yet been established [4]. As other studies reported, the impurities have negative influence on the compatibility with structural materials [5–7]. Therefore, effective reducing method of impurities in liquid materials is required, as well as the online impurity monitor for the system [8,9].

Previous studies related to electrochemical process using a molten salt for tritium recovery from liquid Li were proposed and investigated [10,11]. First, lithium which contains tritium is intimately mixed with a salt mixture of lithium halides in a centrifugal contactor/separator and the tritium in the form of LiT is removed into the salt phase. Second, the salt phase is circulated to an electrolysis unit and the LiT is oxidized to form T_2, which is swept from the salt phase by bubbling helium. Third, the helium is circulated to a clean-up unit which recovers the tritium and removes impurities from the helium gas. Molten salt removal is one of the most promising techniques because it is free from any solid-state diffusion process, which is often slower than in the liquid state [11]. On the other hand, no electrochemical studies for removal and monitoring of oxygen impurities in Li-Pb using chloride molten salt have been conducted yet. In this work, a fundamental transfer characteristics of oxide impurities from lead lithium to chloride molten salt was investigated to explore the potential of this system for removal and monitoring oxide impurities in Li-Pb. Furthermore, these fundamental findings can be expected not only to remove oxygen impurities but also to remove other light impurities such as hydrogen and nitrogen, and to recover tritium by the same method.

2. Experimental

The experimental apparatus is illustrated in Fig. 1. Liquid metal (Li-Pb : Li 0.88 wt%, Atlantic Metals & Alloys, Inc.) was placed in an electrochemical cell in contact with eutectic molten salt (LiCl 58.5 at.% - KCl 41.5 at.%, LiCl: purity 99 %, FUJIFILM Wako Pure Chemical Corporation, KCl: purity 99.5 %, Kanto Chemical Co., Inc.). A stainless steel (type-304) crucible was used. All experiments were performed in a glove box filled with Ar gas which was dried and deoxygenated by a gas purifier. The concentration of moisture and oxygen in the Ar gas were kept to be less than 1 ppm. Before experiment, Li-Pb was melted at first and the slag appeared on the surface of liquid metal was removed at 573 K. Mixed powder of LiCl and KCl for eutectic composition was dried at 423 K for 5 days in the glove box. At the same time, the oxygen due to outgassing was negligible during the experiment because the structural

Fig. 1. Setup of electrochemical cell.

a: Sheathed thermocouple (type K)
b: Li2O feeding tube (SUS304)(C.E.)
c: Glassy Carbon electrode (W.E.)
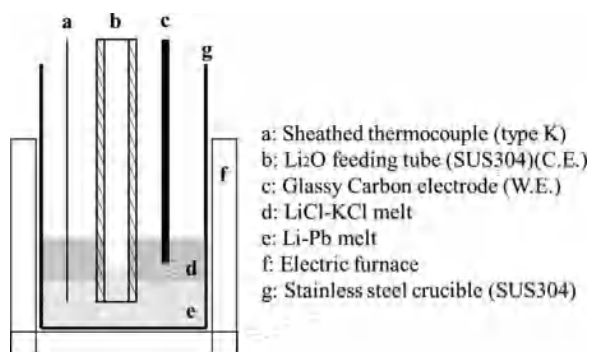d: LiCl-KCl melt
e: Li-Pb melt
f: Electric furnace
g: Stainless steel crucible (SUS304)

material of the crucible (SS-304) had been heated for a sufficiently long time to reduce them. Electrodes of the potentio/galvanostat are connected as shown in the Fig. 1. Li-Pb was used as a counter electrode (C.E.) for cyclic voltammetry. The working electrode (W.E.) dipped in the chloride molten salt was a glassy carbon (GC) rod (φ6.0 mm, Nilaco, the complete length:100 mm, the dipped portion:15 mm). The reference electrode was also Li-Pb and the potential of the reference electrode was standardized against the potential of Li$^+$/Li. Li$^+$/Li-Pb redox potential is measured to be around 0.60 V vs. Li$^+$/Li. The range of potential of cyclic voltammetry in the experiment was from 1.6 V to 2.9 V vs. Li$^+$/Li. The experimental temperature was 723 K. Electrochemical measurements were performed using a potentio/galvanostat (HAB-151, HOKUTO DENKO CORPORATION). Impurity concentration in each liquid was assumed to be uniform due to the mixing by thermal convection. Li2O powder (purity 98 %, FUJIFILM Wako Pure Chemical Corp.) chosen as oxygen impurities, was directly added to liquid Li-Pb through a feeding tube (SUS304). Cyclic voltammetry was performed before the addition of Li$_2$O into liquid Li-Pb. Then, cyclic voltammetry was conducted again after the addition. The change of cyclic voltammogram due to the impurity addition was analysed and discussed. The evolved gases were deduced from the anode consumption with the thermodynamic and electrochemical consideration.

3. Results and discussion

3.1. Monitoring of oxide ions

3.1.1. Without Li$_2$O addition

Fig. 2 shows the cyclic voltammograms (CV) on the GC electrode in the LiCl-KCl melt contacting the Li-Pb melt with different scan rates (0.1, 0.2, 0.5, 1.0, 2.0 V s^{-1}) without Li2O addition at 723 K. CV on the GC electrode in the LiCl-KCl not contacting the Li-Pb (CE: Ni, scan rate: 0.1 V s^{-1}) is also shown in Fig. 2. The current peak did not appear when the molten salt was used as simple substance, but it appeared when contacted with the Li-Pb melt. It was found that the simple substance of the molten salt contained almost no impurities that cause anodic reactions in this range. On the other hand, it was found that Li-Pb contained oxide impurities since the anodic peak current increased at the same potential as when Li2O was added (Fig. 4). The observed anodic currents were considered to be due to the production of carbon dioxide (CO2) on the GC electrode [12–14].

$$C + 2O^{2-} \rightarrow CO_2 + 4e^- \tag{1}$$

The concentration of oxide ions in the LiCl-KCl melt ($C_{O^{2-}}$: mol cm^{-3}) was estimated from cyclic voltammograms for CO$_2$ evolution reaction on the GC electrode (Eq. 1). The anodic peak current for CO$_2$ evolution was clearly observed around 2.5–2.8 V but a cathodic peak was not observed. The peak potential positively shifts with the scan rate. These voltammograms suggest that CO$_2$ evolution on the GC electrode is an irreversible process. The peak current for the irreversible
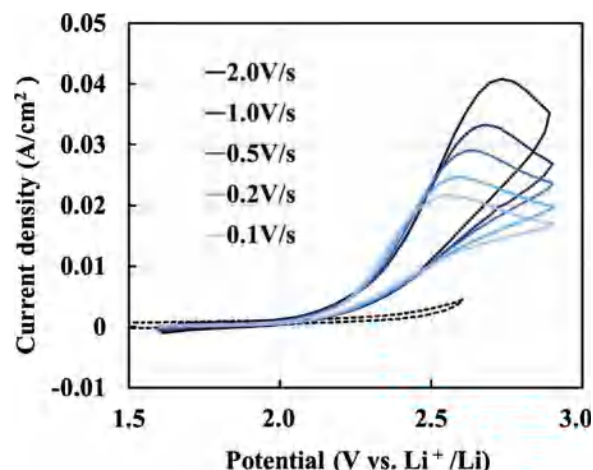

Fig. 2. Cyclic voltammograms with different scan rates (Solid line: 0.1, 0.2, 0.5, 1.0, 2.0 V s^{-1} from the bottom) at 723 K in a eutectic LiCl-KCl melt contacting Li-Pb melt. The dotted line shows the cyclic voltammograms at 723 K in a eutectic LiCl-KCl melt not contacting Li-Pb melt.

case is given by the following equation [12,15].

$$i_p = 0.4958nFC_{O^{2-}}\left(\frac{\alpha nF}{RT}\right)^{\frac{1}{2}}D_{O^{2-}}^{\frac{1}{2}}v^{\frac{1}{2}} \tag{2}$$

Here i_p (A cm^{-2}) is the peak current density, n is the number of electrons transferred in the redox event, $D_{O^{2-}}$ (cm^2 s^{-1}) is the diffusion coefficient of O^{2-}, α is the transfer coefficient of the charge transfer process, and v (V s^{-1}) is the scan rate. The diffusion coefficient for eutectic LiCl-KCl at 723 K: $4.5 \times 10^{-6} \, cm^2 s^{-1}$ was given in Kanzaki's study [16]. To confirm the correlation between the peak current density and scan rate, the peak current densities were plotted against a square root of the scan rates (Fig. 3a). The linear relationship was obtained for each scan rate. In addition, for an irreversible process, the correlation between the peak current density (i_p) and peak potential (E_p) is described by the following equation [12,15].

$$\frac{dln i_p}{dE_p} = \frac{\alpha nF}{RT} \tag{3}$$

Using this equation, αn is estimated from the relationship between ln i_p and E_p. Fig. 3b shows the logarithm of the peak current densities (ln i_p) and the plot against the peak potentials (E_p) in the molten salt. From the slope of these plots, αn was determined to be 0.20. As a result, the concentration of oxide ions in the LiCl-KCl melt ($C_{O^{2-}}$) was calculated to be 0.31 mol% using Eqs. (2 and 3) and the slop of the straight line in Fig. 3a. This value was converted from mol cm^{-2} to mol% by extrapolating the reported density of eutectic LiCl-KCl at 723 K [17]. These oxide ions were primarily transferred from Li-Pb just by contacting the molten salt.

3.1.2. With Li$_2$O addition

Fig. 4 shows the change of CV by Li$_2$O addition. CV after 2 min and 60 min after Li$_2$O addition are shown along with the CV without L Li$_2$O addition. In any cases, 5 scan rates (0.1, 0.2, 0.5, 1.0, 2.0 V s^{-1}) are shown. 210 mg of Li$_2$O was directly fed to 992 g of Li-Pb contacting with 111 g (= 2.0 mol) of LiCl-KCl. The change of anodic current densities caused by the oxidation reaction (Eq. 1) was immediately observed. The transfer of oxide ions derived from Li$_2$O was proved by the change of $C_{O^{2-}}$ calculated by the above method shown in Section 3.1.1 (Table 1). It was considered that this phenomenon was independent of time in minutes because the situation did not change even if it was left for 1 h. In addition, the oxide impurities in the Li-Pb spontaneously transfer to the molten salt. In other words, no power is required to transfer oxide ions to the molten salt.
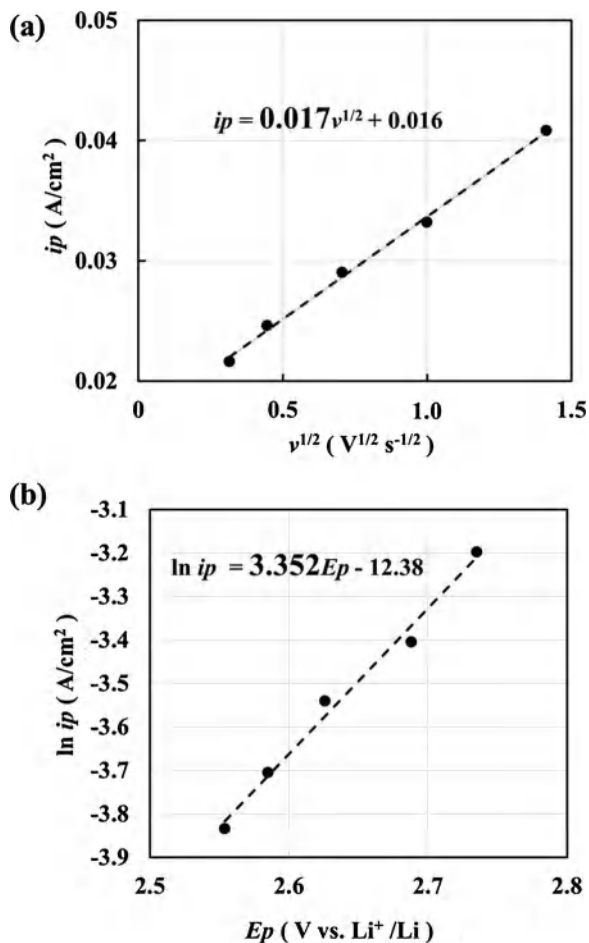
Fig. 3. (a) Peak current densities (i_p) against a square root of the scan rates and (b) logarithm of the i_p against the peak potentials (E_p).
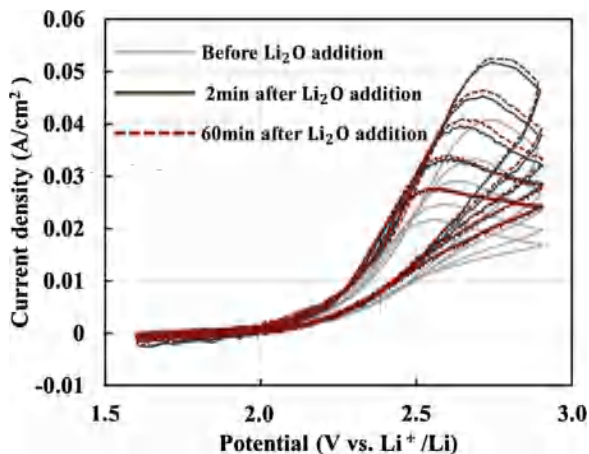

Fig. 4. Cyclic voltammograms with different scan rates (0.1, 0.2, 0.5, 1.0, 2.0 V s^{-1} from the bottom) without and with Li$_2$O addition. (Light solid line: before Li$_2$O addition, Deep solid line: 2 min after the addition, Deep dotted line: 60 min after the addition) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

After this, even if more Li$_2$O (420 mg) were added, no more transfer could be continued. To confirm the saturated solubility, 56 g (= 1.0 mol) of pure LiCl-KCl was added and $C_{O^{2-}}$ was decreased. Then, the decrease of $C_{O^{2-}}$ caused a further transfer of oxide ions. The above results are summarized in the Table 2. This result suggested that the saturated solubility of oxide ions in the molten salt in this system was

Table 1
Change of $C_{O^{2-}}$ caused by Li$_2$O addition.

	Before Li$_2$O addition	2 min after the addition	60 min after the addition
$C_{O^{2-}}$ (mol%)	0.31	0.38	0.38

Table 2
Change of $C_{O^{2-}}$ caused by LiCl-KCl addition.

Amount of LiCl-KCl	2.0 mol	3.0 mol (Just after)	3.0 mol (1 h after)
$C_{O^{2-}}$ (mol%)	0.38	0.25 (0.38 × 2/3)	0.39

about 0.4 mol%. However, the solubility of Li$_2$O in eutectic LiCl-KCl at 723 K: 0.996 ± 0.031 mol% is determined in Tanaka's study [14]. The difference is the subject of future research.

To obtain the maximum amount of spontaneous transferring of Li$_2$O directly added into the Li-Pb, similar experiment was conducted below the solubility. (LiCl-KCl: 167 g, Li-Pb: 496 g, Li2O: 180 mg). As a result, $C_{O^{2-}}$ changed more greatly than before (last time: 0.31 mol% → 0.38 mol%, this time: 0.13 mol% → 0.24 mol%). This result means 103 mg of Li$_2$O was transferred, which was equivalent to 57.2 % (= transfer ratio) of the Li$_2$O addition. The content of oxide impurities in the Li-Pb can be estimated by calculating backward from the transfer ratio and this technique may also be applied to monitoring.

3.2. Extracting of oxide ions

Applying a voltage of 3.2 V (vs. Li$^+$/Li) between GC and Li-Pb was conducted to cause the above reaction (Eq. 1). Thermodynamically, the voltage required to generate CO$_2$ is 1.6 V, but in reality, gas is generated only at 3.1 V or more due to the overvoltage [14]. Chronoamperometry was performed for 45 h, assuming the generation of CO$_2$, the total quantity of electricity was 5210C which correspond to the formation of 0.0135 mol CO$_2$.

Gas evolution was observed on the GC electrode surface (Fig. 5). The consumption of the GC electrode (0.0144 mol) was also observed (Fig. 6). When the electrode was dipped in the molten salt for 45 h without applying a voltage, the reduced mass of the electrode was less than 1 mg, which was negligible compared to the consumption due to electricity. Considering that the GC electrode physically disintegrates in the molten salt, the amount of consumption related to the CO$_2$ generation and the quantity of electricity are considered to be approximately equal. However, the possibility of something other than CO$_2$, such as carbon monoxide (CO), carbonate ions (CO$_3$$^{2-}$) or oxygen gas (O$_2$) generation. If CO was generated, the consumption of the electrode should be double that of CO$_2$, but this was not observed, so CO was not generated or very small even if it was generated. Similarly, the CO$_3$$^{2-}$ formation, which should cause the electrode consumption without gas

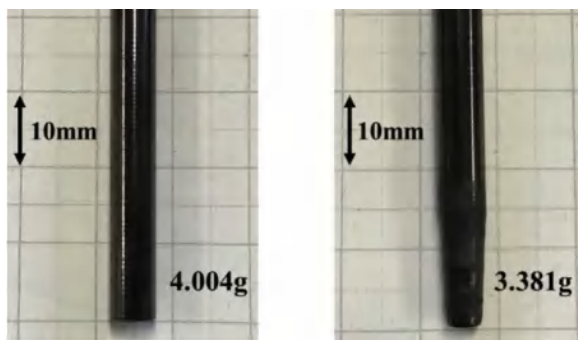**Fig. 5.** Appearance around glassy carbon rod in the molten salt during applying the voltage.

Fig. 6. Photos of glassy carbon electrode (a) before and (b) after chronoamperometry.

bubble formation, was unlikely because gas bubbles were always generated during chronoamperometry. On the other hand, although the over voltage of O_2 gas generation is quite large as in the case of CO_2, the possibility that O_2 is partially generated cannot be completely denied [14]. Another possible cause of the difference of electricity and consumption is the formation of peroxide or perchlorate such as Li_2O_2, $LiClO_4$ or $LiClO$, though their pure substance should be unstable at high temperature [14].

After all, although further investigation is necessary to clarify the anodic reaction, it is certain that oxide impurities can be removed as gases like CO_2. However, according to this result, it takes too much time to remove oxide impurities as CO_2. There is a possibility that the time required for the removal can be shortened by increasing the electrode area or removing it as oxygen. Oxygen gas generation at boron doped diamond electrode has been reported [12]. For practical use of this system, it is necessary to improve the removal efficiency.

4. Conclusion

The transfer of oxide impurities to the molten salt from liquid metal was proved and the possibility of applying the electrochemical method using eutectic LiCl-KCl to reduce and monitor oxide impurities in Li-Pb was suggested. About 60 % oxide impurities in Li-Pb can be immediately transferred to the molten salt just by contacting the molten salt and this spontaneous transferring occurs in minutes. The molten salt can contain oxide ions up to 0.4 mol%, in this work. The content of oxide impurities in the Li-Pb can be estimated by calculating backward from the transfer ratio and this technique may also be applied to monitoring. In addition, the oxide impurities transferred to the molten salt can be removed as gas generation such as CO_2.

CRediT authorship contribution statement

Tomohiro Okada: Conceptualization, Methodology, Validation,

Investigation, Formal analysis, Writing - original draft, Writing - review & editing, Visualization. **Juro Yagi:** Funding acquisition, Conceptualization, Methodology, Validation. **Hiroyuki Miyagaki:** Validation, Investigation, Methodology. **Keisuke Mukai:** Writing - review & editing, Supervision. **Satoshi Konishi:** Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] A. Del Nevo, et al., WCLL breeding blanket design and integration for DEMO 2015: status and perspectives, Fusion Eng. Des. 124 (2017) 682–686.

[2] A. Tassone, et al., Recent progress in the WCLL breeding blanket design for the DEMO fusion reactor, IEEE Trans. Plasma Sci. 46 (5) (2018) 1446–1457.

[3] T. Ihli, et al., Review of blanket designs for advanced fusion reactors, Fusion Eng. Des. 83 (7-9) (2008) 912–919.

[4] H. Tas, S. Malang, F. Reiter, J. Sannier, Liquid breeder materials, J. Nucl. Mater. 155-157 (1988) 178–187.

[5] T. Chikada, et al., Deuterium permeation through erbium oxide coatings on RAFM steels by a dip-coating technique, J. Nucl. Mater. 442 (1–3) (2013) 533–537.

[6] H. Moriyama, S. Tanaka, D.K. Sze, J. Reimann, A. Terlain, Tritium recovery from liquid metals, Fusion Eng. Des. 28 (1995) 226–239.

[7] J.H. Devan, "Compatibility of structural materials with fusion reactor COOLANT and breeder fluids", J. Nucl. Mater. 85 & 86 (1979) 249–256.

[8] T. Flament, P. Tortorelli, V. eoen, H.U. Borgstedt, "Compatibility of materials in fusion first wall and blanket structures cooled by liquid metals", J. Nucl. Mater. 191-194 (1992) 132–138.

[9] S. Malang, P. Leroy, G.P. Casini, R.F. Mattas, Yu Strebkov, Crucial issues on liquid metal blanket design, Fusion Eng. Des. 16 (1991) 95–109.

[10] H. Moriyama, Y. Asaoka, Y. Ito, Kinetics of tritium recovery from liquid Lithium by molten salt removal, Fusion Sci. Technol. 19 (1991) 1046–1050.

[11] H. Moriyama, et al., Tritium recovery from liquid metals, Fusion Eng. Des. 28 (1995) 226–239.

[12] Y. Kado, T. Goto, R. Hagiwara, Thermodynamic and kinetic properties of oxide ions in a LiCl-KCl-CsCl eutectic melt, J. Electrochem. Soc. 160 (9) (2013) E90–E93.

[13] Y. Kado, T. Goto, R. Hagiwara, Dissolution behavior of Lithium oxide in molten LiCl-KCl systems, J. Chem. Eng. Data 53 (2008) 2816–2819.

[14] T. Tanaka, et al., Anodic reactions on some materials in LiCl-KCl melt, ECS Trans. 50 (11) (2012) 127–134.

[15] R.S. Nicholson, I. Shain, Theory of stationary electrode polarography. Single scan and cyclic methods applied to reversible, irreversible, and kinetic systems, Analyt. Chem. 36 (4) (1964) 706–723.

[16] Y. Kanzaki, M. Takahashi, The oxygen electrode in fused lithium chloride-potassium chloride eutectic containing oxide ion, J. Electroanal. Chem. Interfacial Electrochem. 58 (2) (1975) 339–348.

[17] H. Ito, Y. Hasegawa, Y. Ito, Densities of eutectic mixtures of molten alkali chlorides below 673 K, J. Chem. Eng. Data 46 (5) (2001) 1203–1205.