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Electrochemical hydrogen detection in DONES loop materials

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ABSTRACT

The radiation-induced degradation of materials in fusion systems is planned to be investigated in IFMIF-DONES (*International Fusion Materials Irradiation Facility - DEMO Oriented Neutron Source*), where fast neutrons are produced by a reaction of deuteron-beams with a liquid lithium target. A by-product as critical impurity is hydrogen, which might affect the reliable and safe operation of the IFMIF-DONES loops. Therefore, an important issue is the measurement and control of the hydrogen impurity concentrations in liquid lithium.

Initially, a practically applicable direct measurement of hydrogen concentrations in lithium facilities did not exist. However, one promising approach to manage this issue is based on the electrochemistry of the DONES materials The developed Electro-Chemical Hydrogen Sensor for Liquid Lithium (ECHSLL) allows the measurement of the electromotive Force (EMF) between a reference materials system and the loop lithium melt, and thus the monitoring of the hydrogen impurity concentrations.

This article will show backgrounds of non-metallic impurities in liquid metal materials and the specific material stabilities within DONES. Liquid lithium is a very reactive material. Therefore critical issuesareviable materials compatibilities, the interactions with hydrogen and the transport behaviour of H-ions in electrolytes at the applied temperatures. Further issues are also the syntheses of the electrochemical materials, as hydrogen conducting electrolytes, reference electrode systems and the different procedures (heat treatments and conditioning steps). The tests showed the functionality of the developed H-sensor. Beyond that, the used material combinations exhibited reliable behaviour in melts under harsh conditions. Hence, the most critical aspect (stability of the sensor materials in the Li-melt) has been resolved by using niobium sensor heads. The observed experimental EMF potentials are in good accordance compared with calculated models, also in long-time experiments.

1. Introduction

Materials in nuclear fusion power plants will be exposed to extreme strains and impacts due to the applied conditions such as high temperature and especially the generated irradiation by neutrons with energies of 14 MeV. For the investigations of such critical issues and for generating the material-related knowledge in advance, the DEMO fusionenergy irradiation can be made available by a special approach of nuclear chemistry (but of course without an output of a surplus in energy balance). Indeed, IFMIF-DONES, the *International Fusion Materials Irradiation Facility - DEMO Oriented Neutron Source*, is such a facility to investigate materials under DEMO conditions [1]. The engineering design of IFMIF-DONES is currently performed under a WPENS (Work Package Early Neutron Source) project in the framework of EUROfusion activities. The medium-term European realization of IFMIF is called DONES. It will be constructed in Escuzár, near Granada/Spain and is based on the principles of IFMIF. It differs only by several deductions, e. g. only one 40 MeV-Deuteron accelerator (see orange box in Fig. 1) [2–5].

The generation of a 14 MeV neutron ray results from a collision of the accelerated deuterons with a liquid lithium target. As consequence, protium, deuterium and tritium atoms accumulate in the lithium. In IFMIF-DONES only the neutrons are the focus of interest. They interact with material specimens in the test cell (TC), whereas the generated hydrogen isotopes (Q_2 for the sum of all isotopes) are not consumed (as by a fusion reaction). Therefore, the hydrogen isotopes must be considered as continuously generated impurities. In contrast to DEMO, hydrogen remains in the lithium system until it is removed by an yttrium based hydrogen hot trap, which forms a central part of the impurity control system (ICS) of DONES [6].

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With regards to material properties such as reliability, stability and compatibility, the fact that lithium is a very reactive material becomes an important aspect [6,7]. Materials stable in pure lithium, underlie significant corrosion and embrittlement in presence of gaseous impurities such as hydrogen. Unfortunately, this issue also applies to steel alloying elements and hence to the steel alloy based structural material used for the DONES loop walls [8].

1.1. Hydrogen vs. DONES materials

The hydrogen content in the IFMIF-DONES loop needs to be strictly controlled by an impurity control system (ICS) which forms a crucial part of the DONES instrumentation [9]. As consequence, a sensor had to be developed with the aim to generate a signal as direct consequence of its material properties (and their changes). This directly leads to questions about the reliability and compatibility of the used materials; functional materials affecting the sensor surfaces and the internal material compatibilities of the sensor components.

2. Experimental

2.1. General sensor principles

The applied practice of electrochemical measurements is strongly dependent on the interaction between materials [10]. The electrochemical potential E of a redox binary system in electrochemical equilibrium is dependent on the effective concentration (also known as its activity a) of its oxidized compound (a_{ox}). In case of diluted systems concentration and activity are equal. The unique main approach to get an ascertainable physical signal of the potential E (voltage) is the Nernstequation [11]:

$$E = E_0 + \left(\frac{\mathrm{RT}}{\mathrm{nF}}\right) \ln \frac{[\mathbf{a}ox]}{[\mathbf{a}red]} \tag{1}$$

Eq. (1). Sketch $E_0=$ standard potential, R= gas constant, n= valence, F= Faraday constant.

The base principle of EC sensors is to detect the difference of two

potentials, which occur by an interface of two systems, separated by an intersection of an electrically non-conductive, but ion-exchanging material. In EC cells the measurement is based on *net processes* [12], and for dissolved hydrogen <1> transforms to <2> [13]:

$$\Delta E = \left(\frac{\mathrm{RT}}{\mathrm{nF}}\right) \ln \frac{[\mathrm{H}diss]}{[\mathrm{H}sat]} \tag{2}$$

Eq. (2). $[H_{diss}] =$ hydrogen dissolved in lithium, $[H_{sat}] =$ saturated hydrogen-Li-melt.

Hydrogen dissolved in liquid lithium $[H_{diss}]$ exceeding the saturation concentration $[H_{diss}]$, precipitates as LiH, which stands for the reduced ion species in Eq. (1). By this definition, the content of the species in question $[H_{diss}]$ is directly accessible to experiments: only $[H_{diss}]$ is an unknown quantity. It can easily be resolved using experimental data: ΔE is measured as the Electromotoric Force (EMF), a voltage.

 $[H_{sat}]$ must sustain a permanent potential by a suitable balance reaction, to serve as long-term stable reference electrode (RE). In most cases, a RE is a liquid solution of an ion species in presence of a close related dissolved compound (e.g. salt), whose concentration is high above the saturation concentration, i.e. the RE solution it is always supersaturated. This guarantees a reference functionality along the applied temperature range. This enables always the sure and reliable comparison with a diluted experimental system. For this reason, the development of a sensor should be considered as materials science. The saturation concentrations are not reached in DONES lithium looops [6].

2.2. H-sensor materials aspects

Literature research indicates, that the development of an impurity sensor for liquid lithium (LL) is a more challenging task than for nearrelated liquid metal systems as liquid lead, liquid lead–bismuth or lead–lithium [12,14]. The huge number of possible sensor materials, which are stable in those systems, is drastically reduced using LL melts [7,15,16]. Furthermore, in contrast to the alkaline homologue sodium, the high reactivity of lithium with metal oxides excludes all approved sensor systems based on oxides of zirconia, yttrium and alumina [17,18,19]. However, in future these materials might move into the



Fig. 1. Sketch of the IFMIF-DONES [1] with the Impurity Control System (highlighted by a green frame); orange frame: differences between IFMIF and DONES.

focus of investigation for their application in LL [20]. At present the remaining smal number of LL-stable materials is reduced by gaseous impurities as hydrogen. Additionally a sensor must fulfill some more selective preconditions: permeability for the detectable species, material availability and also the possibility of moulding into the required functional lay-out. As consequence, a relevant EUROfusion WPENS-task was launched in this regard: development of an Electrochemical Hydrogen Sensor for Liquid Lithium (ECHSLL).

Under practical handling conditions and RAMI aspects (especially maintenance and inspection, i.e. assembly, application, re-use), a sensor should be conceived as single-rod measuring cell (SRMC). This prevents any problems which might arise by undefined deviations between the two electrode sides (caused by low pressures, shear forces in the LL stream). Furthermore, a SRMC has only one electrode surface in contact with the lithium melt.

2.3. ECHSLl

Fig. 2 shows a cross section scheme of such a sensor design. Detailed technical details of the ECHSLL are given elsewhere [21]. The focus of this work is therefore placed on the discussion of the functional materials, which are used for the ECHSLL device. The current concept of the sensor consists of the following main parts and materials:

the niobium membrane material (Nb MM),

- the hydride-conducting eectrolyte (HCE),
- the reference electrode (RE) system.

2.3.1. The niobium membrane

Niobium consolidates: a) the mechanically and chemically stable vessel, b) a hydrogen ion (hydride) permeable membrane, c) as electrical electrode contact. It is the material in main contact with the aggressive/harsh liquid lithium medium. Therefore the chemical compatibility with LL + impurity is the most critical and decisive requirement [15,22–24]. Under DONES-related conditions, niobium was evaluated as the most suitable material [25,26].

With regard to purely technical and physical parameters only Tantalum seems to be a better membrane material at first sight. However, it is significantly less reliable, It is more difficult to form into the required sensor shapes. Furthermore, Ta affrected by Li melts is more sensitive to various impurities [22,27]. Therefore, niobium is first choice for this subject (Fig. 3).

2.3.2. Hydride-conducting electrolyte HCE

An electrochemical sensor is based on a material (i.e. ionic species) conducting interface, enabling a charge transfer to generate the measured potential difference. The HCE material must be compatible with its vessel material and must exhibit a sufficient wetting with the interfaces. The two-phase diagram of the HCE system, CaCl₂ + CaH₂ shows an eutectic at 20% Ca-chloride with a melting point of 624 $^\circ C$ [28]. For many practical reasons it would favourable to work with that low melting point. However, due to the properties of the different H-ion types (H⁺, H⁰, H⁻), only low percentages of CaH₂ in this HCE-system allow the needed hydride conductance (5% CaH2, mp = 823 $^{\circ}$ C). Higher ratios as in the eutectic support only the proton conductance. Liquid Lithium strongly supports the polarization of dissolved hydrogen to hydride, therefore the ion-transfer medium must maintain the hydride conditions. At temperatures in the Impurity Control System (ICS) of IFMIF-DONES, the HCE is not liquefied. Hence, it acts as a solidelectrolyte.

The performance of this HCE, namely complete wetting the Nbsurfaces is a decisive criterion for the sensor function. During the HCE-melting process shrinking of the calcium-salt mass, formation of hollows and cracks in the HCE bulk might cause failures or insufficient sensor functions (under auspicious conditions these issues can be solved by a repeated temperature conditioning step).

2.3.3. The reference system

The reference electrode (RE) for ECHSLL consists of lithium with an oversaturation of hydrogen by LiH in high excess (Li + LiH). This which means a mole ratio H/Li = 1:2 resp. 33 at% (compared to H-saturation in LL at 300 °C: 0,344 at-%). This RE system is stable up to 685 °C [29]); above 685 °C solid LiH becomes fully soluble in LL disabling any discrete RE function.



Fig. 2. Sketch of the ECHSLL-SRMC design.



Fig. 3. Niobium membrane material, 600 µm thickness.

2.4. ECSLL functionality

For the hydrogen monitoring in liquid lithium, finally following chemical compounds are functional materials of the ECHSLL cell (Fig. 4):

- The membrane Nb < 600 µm,
- The melt: Li + H_{diss},
- The electrolyte: 0,95 eq. CaCl₂ + 0,05 eq. CaH₂(5%),
- The reference: $0,5eq Li + 0,5eq LiH + H_{sat(T)}$,

With the definitions $Li + H_{diss} = H_{Li}$ resp. $Li + LiH + H_{sat} = H_{RE}$ with Nb-membranes, the cell is thereby:

H_{Li} // Nb // HCE // Nb // H_{RE}

The driving force and the direction of ion-flow is pushed by lithium; it has the highest negative EC standard potential of all elements [30].

 $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-\text{E}_0 = \textbf{-3,04} \text{ V}$

This strong reduction-force compel dissolved hydrogen to polarize to its hydride. On the reference side, due to the permanent supersaturation of its LL phase, the hydride ions react discharging with lithium.

As applied in the RE, LiH reversibly dissolves in LL, which can generally be used to display exactly predefined H-concentrations; as long as final concentrations are under saturation (at 300 °C 0,344 at% \equiv

17,85 mg on 10 g Li [29]). ECHSLL acts as concentration cell, and saturation in DONES will not be reached, therefore measured voltages are the result of the hydrogen ratio test melt/RE melt. Besides the fact that the whole EC-cell configuration is very symmetric; this avoids disturbing polarization incidents as far as possible. This is a strong material-based surplus for the reliability of this sensor design.

2.5. Technical set-up and instrumentation

The current set-up is laid-out to enable three different simultaneous measurements. The data acquisition is meanwhile executed by a specially adjusted multiplex voltmeter system (IVIUM-Vertex), Fig. 5.

Based on practical experience in LL experiments by Konys [31], work with Li-melts is carried out under established security regulations [32]. So far, the experiments included durations of several hours, one day (resp. 24 h) up to a few days. For security reasons long-term tests of several weeks were carried only at 300 $^{\circ}$ C.

3. Results

Measurements were carried out in a temperature range from 250 up to 500 $^{\circ}$ C in stagnant solutions (until a loop-system can be applied). Although temperatures in the DONES ICS will not be above 300 $^{\circ}$ C (due to the use of cold trap devices). However, with the aim to prove stability and effects also under explicitly "harsher conditions" (Fig. 6) ECHSELL tests were carried out at KIT at higher temperatures as well (Fig. 6). In any case, the Nb-membranes immersed into LL and the H-Li melts did



Fig. 4. Functional Materials of ECHSLL.



Fig. 5. Test-stand configurations (circuit).



Fig. 6. Calibration curves for 250 °C up to 500 °C; inlay: Li-melt with $H_{Li} = 50\%$ of H_{sat} at 300 °C.

not suffer any damage caused by corrosion or dissolution or cracks.

Because the solubility of hydrogen in lithium quickly change with temperature, H-saturation values for different temperatures are achieved by different amounts of added hydrogen. Due to equation < 2>, annealing a given concentration will result in significantly higher EMF (Fig. 8). Vice-versa, cooling down a hot melt leads to a quick supersaturation (which indeed can be used to remove "H-precipitate" (LiH) from melts at lower temperatures).

A transfer of 10 mg of a fully saturated Li-H melt specimen of 10 g at 300 °C into the same amount of pure lithium theoretically results in a 1000-fold dilution (1/1000 of 0,344 at%, = 3,44 ppm). At the moment, this value seems to be the lower detection limit of the sensor. The uncertainty of measurement is always dependent on suppliers data of

impurities (<1 ppm for Li from American Materials ®).

An interesting recognition was, that different lithium melt specimen with low H-concentrations stored at room temperature (in closed sealed and inert boxes) showed reddish or violet precipitates after mid-term time (Li₃N). However, specimen always maintained a well metallic silvery appearance if containing dissolved hydrogen (>20 % of H_{sat}). This evidently means, that higher H-contents significantly sustain well metallic properties, by avoiding reactions with other impurities (in this case dissolved H reacted with nitrogen to NH₃). Those specimen could re-used as Li melts.



Fig. 8. EMF as f(T), T-increase from 300 °C to 500 °C.

4. Summary and outlook

An electrochemical sensor was designed and constructed for detecting hydrogen impurities in liquid lithium IFMIF-DONES. The demanding challenges to elaborate an electrochemical output of materials and their combinations under the highly aggressive operating conditions in the liquid lithium melt successfully were resolved. The sensors work properly and indicate EMF values in such good accordance with the adjusted hydrogen concentrations, that calibration curves could be established.

As future options sensors with drastically thinner membranes of 0.4 down to 0.3 mm are to be manufactured in combination with general lower sensor sizes. Furthermore, dependent on the purposed application, the current design furthermore allows the use of different sensor connections/features/flanges.

Those sensors initially had been designed for the measurement of general hydrogen contents (" Q_2 "). A distinguished *electrochemical* detection of protium, deuterium and tritium by ECHSLL will be a huge challenge (because of their identical electrochemical properties). However varied concepts using known physical effects (varied membrane sizes, different distinctive shapes etc.) seem to be a promising approach for the design of a EC(P,D,T)SLL sensor. Furthermore, procedures using ECHSLL for a directed hydrogen permeation enabling removal by potentiostatic measures (hydrogen pumping) by an Active Electrode Operations (AEO) modus are currently under investigation.

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.

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