



Detection of hydrogen as impurity in liquid lithium: An electrochemical hydrogen-sensor for IFMIF-DONES

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ABSTRACT

IFMIF-DONES, the International Fusion Materials Irradiation Facility - DEMO Oriented NEutron Source, is the planned facility in Granada/Spain for fusion materials investigations using neutron irradiation in the scale of DEMO-oriented energies. This irradiation is generated by the interaction of deuteron beams with a liquid lithium flow-target system, containing huge amounts of this very reactive alkaline-metal. An important and critical issue during the operation of IFMIF-DONES is the enrichment of dissolved impurity components in the Li-melt and in the liquid melt concerning reactivity, corrosivity and radiation hazards. In the case of hydrogen, there is the danger of H-introduced embrittlement of the loop structure components as well as effects and hazards of the radioactive tritium. The application of liquid lithium in the scope IFMIF-DONES unconditionally hence requires a suitable impurity control.

Regarding this subject, an electrochemical sensor for a continuous hydrogen monitoring is being developed in the frame of an international EUROfusion-WPENS task. This sensor was designed as single-rod-measuring-cell with niobium as the relevant membrane-material and a hydrogen conducting electrolyte. Potentials (Electro-Motive Force EMF) are being measured between the Li melt and a reference electrode by voltmeters with high impedances and can easily converted into H concentrations. Long-term tests (campaign-units of several hundred hours) in stagnant Li-melts with different sharply controlled hydrogen concentrations showed, that the sensor fulfills the requirements of chemical and mechanical stability and functionality also under harsher conditions (temperatures up to 500 °C). The obtained results and operational experiences will be discussed, e.g., concerning application windows, reproducibility and calibration needs. Additionally, recommendations will be outlined for upgraded systems and future qualification needs.

1. Introduction

IFMIF-DONES is the International Fusion Materials Irradiation Facility - DEMO Oriented NEutron Source, facility. Its engineering design is being performed under a WPENS project (Work Package Early Neutron Source) in the framework of EUROfusion activities, and will be realized near Granada/Spain [1,2].

In this facility, neutrons with DEMO-like energies of 14 MeV are generated in a target system by a 40 MeV initiated D-Li reaction, and interact with specimen of foreseen DEMO materials in the test module (Fig. 1).

Owing to the D-Li splitting reaction the core lithium loop of the test cell will enrich with hydrogen mainly both from the lithium target system and the deuteron beam [3]. But in contrast to fusion reactors, production and reactions of hydrogen are not the main purpose of DONES. This makes hydrogen being an impurity. This is a very critical issue, because it affects materials as steels by embrittlement and fatigue stresses, leading to system failures. Furthermore, the corrosivity of the aggressive alkaline-metal lithium [4] is additionally enhanced by hydrogen: the durability of materials in pure liquid lithium is degraded

in presence of hydrogen [5,6].

This requires a solid knowledge of the hydrogen content to be measured by reliable diagnostic systems in the Impurity Control System (ICS) of IFMIF-DONES, beside other occurring impurities, especially nitrogen [7]. The special requirements and specification of an impurity monitoring system within a complex lithium facility (i.e., small sizes, short ways, robustness, long-lasting lifetimes, on-line monitoring and minimal response times [8]) are a typical feature and excellence of electrochemical techniques [9]. This subject constituted the development of an ElectroChemical Hydrogen Sensor for Liquid Lithium (ECHSL) within the frame of an EUROfusion WPENS task.

Sensor and related monitoring system were designed to detect hydrogen contents using a well-defined and stringent correlation between concentration and electrical output. The general design and primary device geometries are described in detail elsewhere [10]. In this article the results obtained in the actual test campaign will be discussed concerning sensor functionalities, application of different test melts and current practical considerations.

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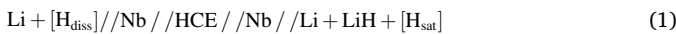
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2. Experimental

2.1. General sensor principles

The sensor function is based on the formation of an electrical potential, the Electro-Motive Force EMF, between two different chemical systems [11]. It is an electrode set-up consisting of a working electrode (WE) in contact with the investigated lithium melt (concentration $[H]_{Li}$), and a reference electrode (RE) with fixed and known H-concentration. The RE is based on a chemical system in a stable steady-state condition, in this case Li saturated by hydrogen with the concentration $[H]_{sat}$, in presence of LiH to stabilize permanent super-saturation. WE and RE are separated by a dielectric electrolyte medium. Thus, only an ion (proton) flow can take place between the electrodes, resulting in a potential difference between RE and WE, measured by a high impedance voltmeter.

In liquid lithium such techniques never were applied before, although several (mainly anion based) concepts are established for electrochemical impurity measurement in liquid metal technologies [12–13]. First step to realize such a sensor is the definition of an electrochemical cell, using $CaCl_2+CaH_2(5\%)$ as Hydrogen Conducting Electrolyte (HCE) as seen in Fig. 2:



With $Li + [H_{diss}] = [H]_{Li}$ and $Li + LiH + [H_{sat}] = [H]_{RE}$ the cell interfaces are:



An advantageous issue is the chemical relationship between Li-melt and RE system; only the concentration $[H]_{Li}$ is an unknown parameter in (2). This gives occasion to determine the experimental concentration using the Nernst-Equation, measuring the potential E in relation to a known reference concentration (3)

$$E = E_0 + \left(\frac{RT}{nF}\right) \ln \frac{[c]_{unknown}}{[c]_{reference}} \quad (3)$$

And because the measurement is based on net processes [14], Eq. (3)

simplifies to

$$\Delta E = \left(\frac{RT}{nF}\right) \ln \frac{[H_{diss}]}{[H_{sat}]} \quad (4)$$

All sensor components have to resist the harsh lithium environment. Ceramic materials (as zirconium-based perovskites) are very good hydrogen conductors, and therefore would be the first choice for electrochemical hydrogen-sensor devices, but unfavorably ceramics are unstable in lithium (which counts generally for any other metal-oxide and metalloid-oxide material) due to the high reduction power of lithium metal (which is the highest one for chemical elements).

Niobium is one of the few membrane materials convenient for measurements in lithium; it combines chemical and mechanical stability with one of the highest hydrogen permeabilities. Therefore, for ECHSL niobium was selected as the standard membrane material for both the Working Electrode (WE) and Reference Electrode (RE).

2.2. ECSLL chemical preparation

A mixture of $CaCl_2$ and CaH_2 is described by Sridharan et.al [15], as suitable Hydrogen Conducting Electrolyte (HCE). The properties of this HCE are variable in a by the ratio $CaCl_2/CaH_2$ to adjust its final function (hydride or proton conductor). Only low concentrations of CaH_2 as 5 at % will support hydride conduction. This Ca-chloride/hydride ratio (amounts of 16.6 g) was defined as standard HCE-load for all experiments (size of the niobium WE-head: outer diameter = 20 mm, height = 40 mm, wall thickness = 600 μm). $CaCl_2$ and CaH_2 , both of reagent grade 99,99%, were supplied from Sigma-Aldrich®.

The performance of the sensor is strongly dependent on the HCE preparation, and its synthesis has proven to be the most important step in the sensor manufacturing process. The adjusted Ca-salt mixture is to be conditioned by heating to 50 K above its melting point of 823° This annealing step initiates a chlorine-hydrogen exchange forming $CaHCl$. This drastically increases the hydride conductance at lower operation temperatures (300 °C).

The RE was loaded with an equimolar mixture $Li + LiH$ (0.7 g Li and 0.8 g LiH, powder grade –30 mesh). The RE sizes are: outer diameter =

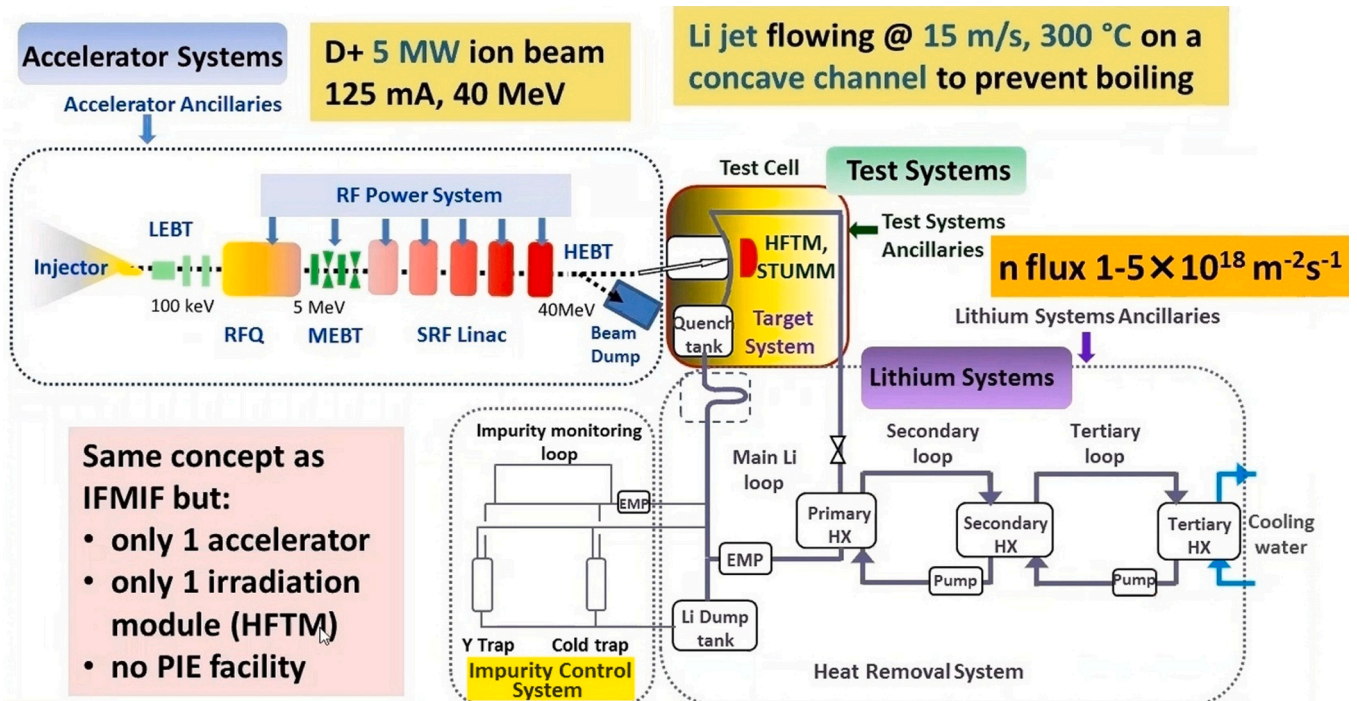


Fig. 1. Scheme of the IFMIF-DONES facility. Hydrogen measurement and monitoring will take place in the loop of the Impurity Control System.

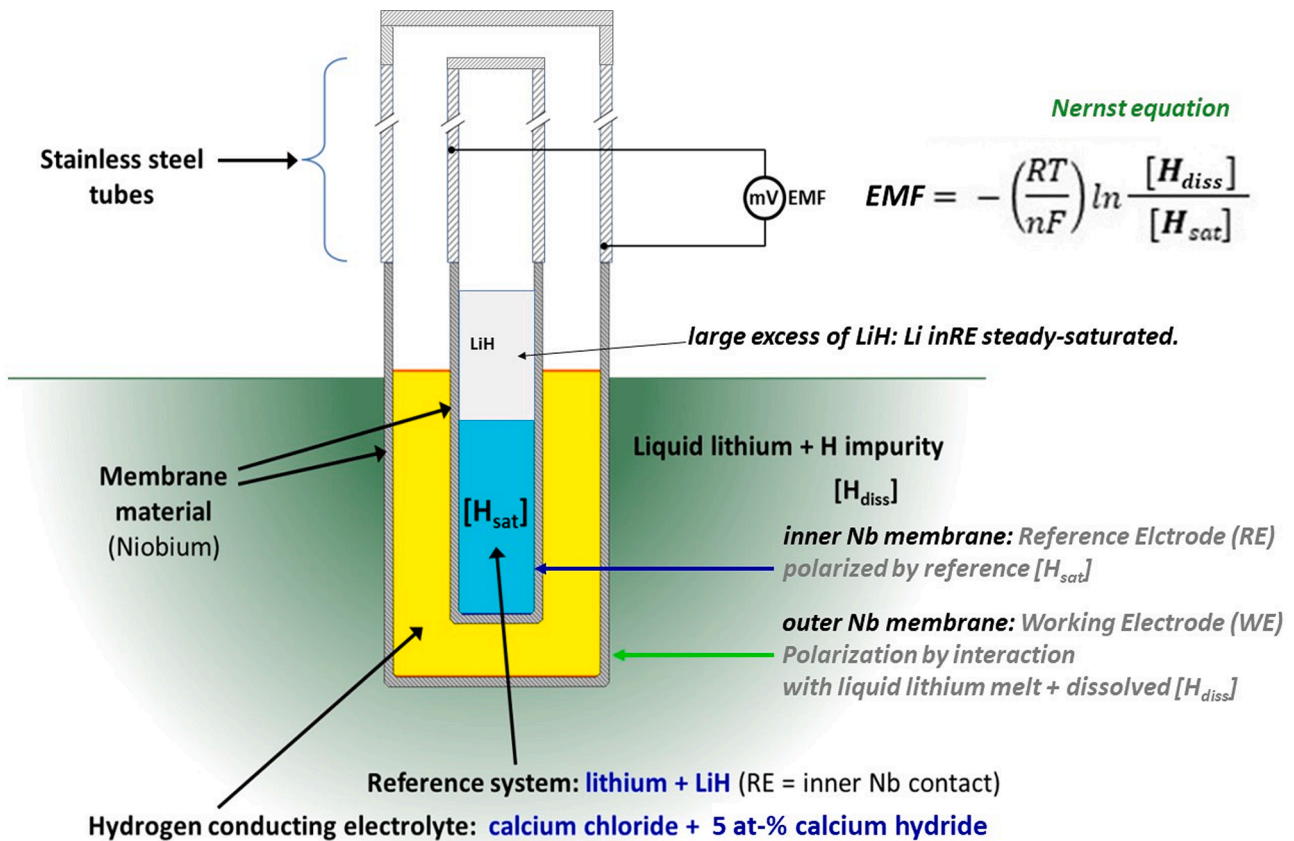


Fig. 2. ECHSLL sensor, layout as single-rod electrode design; WE in contact with the lithium melt.

8 mm, wall thickness = 600 μm , height = 35 mm). Both RE-chemicals a) are oil-free lithium (packaged under argon, supplied from American Elements/MERELEX[®], impurities referring to the certificate of analysis < 1 ppm) and b) LiH from Sigma-Aldrich[®], reagent grade 99.99%.

The high excess of LiH in the RE guarantees a permanent temperature-dependent hydrogen saturation [16,17], fixing a stable correspondent reference potential. LiH dissolves reversibly in liquid lithium [18]. This effect was used to adjust and control the effective experimental hydrogen concentration in the lithium melts by adding the desired LiH amounts [19].

2.3. ECSLL assembly sequence

The loading of the sensor WE and RE by the reagents has proven to be challenging due to geometrical and material reactivity conditions. Homogeneous dense and pore-free filling is required and the reactants have to be in optimal, well-wetting contact with the Nb-walls. Avoiding cracks in the electrolyte is an essential topic. To exclude any deficiency in the WE and RE loads, every prepared sensor is heat-treated with 500 $^{\circ}\text{C}$ prior to use (min. duration 1 h). Most important effect is to achieve saturation dissolution of hydrogen in the RE lithium part. Without such a conditioning step, the WE primarily measures against undefined RE concentrations, and in consequence, erratic EMF values might be indicated, as long as a stable RE condition $[H_{sat}] = [H]_{RE}$ is achieved.

Sensor preparation and implementing of experiments followed a strict sequence:

- 1) Loading of HCE mixture in ECHSLL WE-tube.
- 2) Settling/degassing procedures of the HCE mixture.
- 3) WE-assembly annealing at 875 $^{\circ}\text{C}$.
- 4) Cooling interval (2 K/min).

- 5) Loading of lithium in RE head at $T \sim 220^{\circ}\text{C}$.
- 6) Control of Li position in RE-head (dipstick).
- 7) Loading and settling of LiH in RE head.
- 8) Conditioning of the sensor head up to 500 $^{\circ}\text{C}$.
- 9) First use in Li melts with sufficient lead times at constant temperature (ca. 24 h).

The applied total length of 250 mm (9.8 in.) revealed to be the maximum suitable and manageable size working under glovebox conditions (Fig. 3). The sensor is modularly designed for adjusting the layout easily to upcoming needs triggered by testing results or future application requirements. Beside different flange designs, this especially counts for membrane material properties (thickness, diameter, RE-WE distance).

All laboratory experiments have to be carried out in a dry argon atmosphere unconditionally with a high-temperature nitrogen getter-device (in our case the MB20G system from MBRAUN[®], Munich/Germany). Without nitrogen elimination, the investigated lithium melts itself would undesirably act as effective nitrogen getter forming Li_3N , which might drastically affect the Li-melt properties and H-concentrations.

3. Results

For sensor testing Li melts of 10.0 g (18.8 ml) were heated up to 300 $^{\circ}\text{C}$ in stainless-steel crucibles (steel 1.4571) and the sensors were slowly immersed with the niobium heads into the lithium melts only in such depth, that any direct contact of the steel structure with the Li-melt is being excluded (to avoid Fe-Li-Nb mixed potentials).

The temperature control was achieved by specially manufactured Li-stable thermo-couples (from TCdirect[®]) embedded in the Li melts with 5–7 mm distance to the WE head. Long-term dwell time experiments

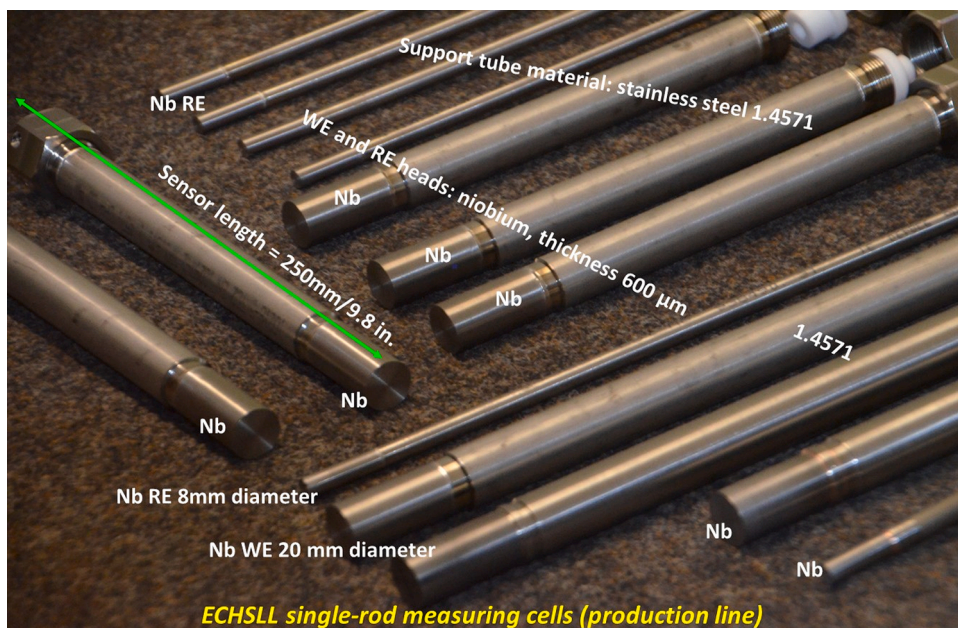


Fig. 3. ECHSLL devices, main size 25 cm, diameter 20 mm (RE size 8 mm).

were carried out in heating capsules with lithium melt amounts up to 60 cm³

EMF measurements based on dielectric electrolytes require voltmeters with highest possible internal resistances R_i . This was achieved

using voltmeters of the type Keithley series K2002 (from Tektronix Corp. ©) with $R_i = 100 \text{ G}\Omega$ (and 8.5 digits). For stable signals sufficient lead-times (range of 10 h) are to be temporized, whose durations are in the frame of comparable experimental set-ups and values mentioned in

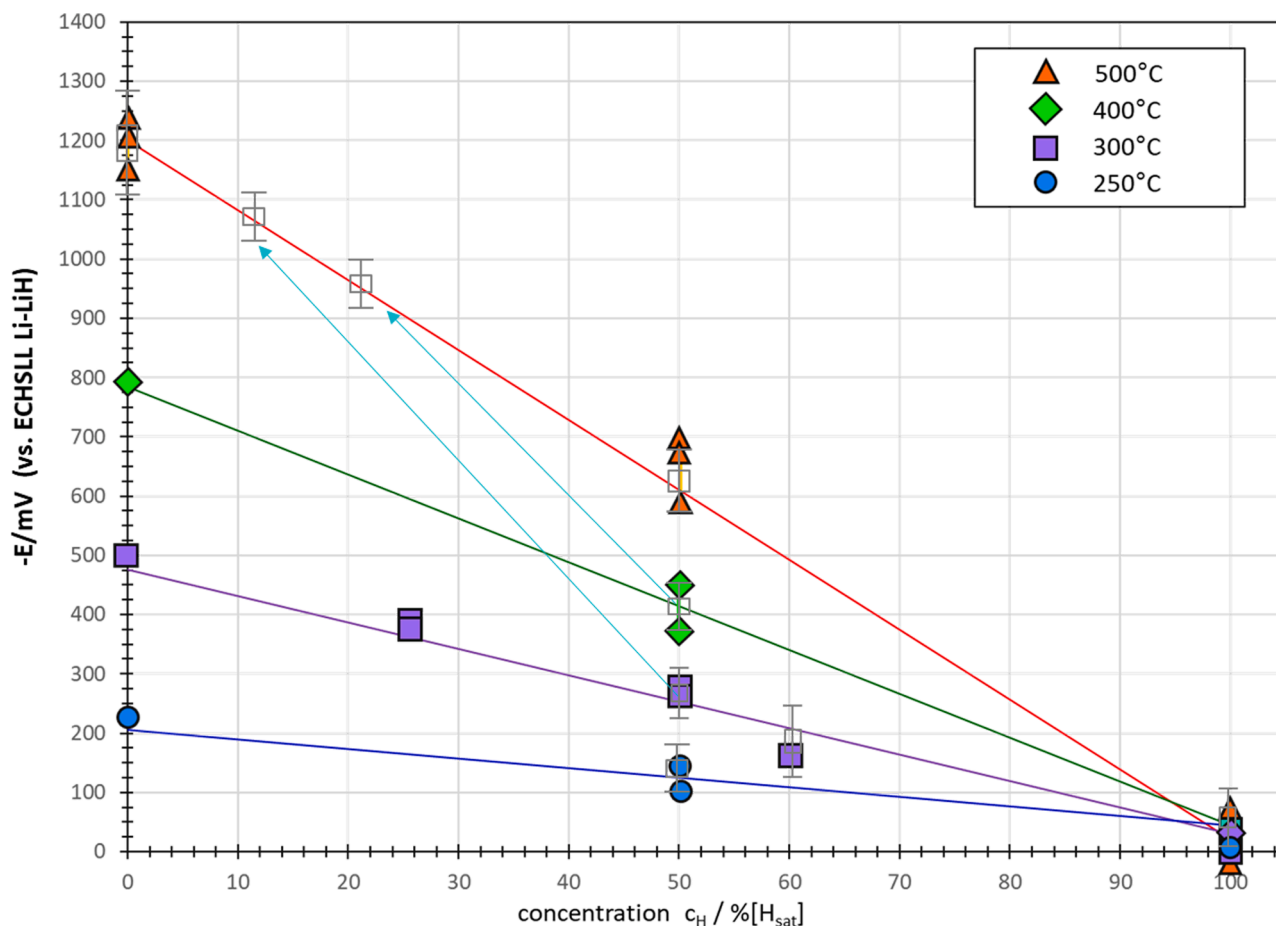


Fig. 4. EMF as function of [H]Li for Li-melts with temperatures of 250, 300, 400, 500 °C.

[19]. EMF values were defined as stable, when ground noise oscillations were lower than 5% of the average EMF values at 300 °C. With rising temperature the ground noise increased (10–15% of EMF at 500 °C). This mainly can be led back to the heating intervals holding the target temperature, in combination with the significant change of hydrogen solubility with the temperature (hence influencing the EMF): it increases about a sevenfold between 200 °C and 300 °C, and a fourfold between 300 °C and 400 °C [4,16,17].

For calibration-curves concentrations of $c(\text{H}) = 0$, $[\text{H}]_{\text{Li}} = 50\%[\text{H}_{\text{sat}}]$ and fully saturated $[\text{H}_{\text{sat}}]$ were set as anchor points and served as orientation for further experiments. Measurements proved the chemical stability of the ECHSLL system also at higher temperatures (> 300 °C as it is necessary for the sensor conditioning). Indeed, the DONES operation temperatures are “only” 250–300 °C, especially in the Impurity Control System.

For every temperature-series the sensors were immersed in pure lithium, and then the target concentrations of the melt were adjusted by adding correpodent LiH analogue to [19]. The EMF shift of given fixed concentrations $[\text{H}]_{\text{Li}}$ at 300–400 °C under varied temperatures was also investigated showing drastic EMF increase due to the mentioned high increase of H-solubility between 300 °C and 500 °C.

Fig. 4

For long-term measurements, the sensors were immersed into the melts with a $[\text{H}]_{\text{Li}} = 0.6 \times [\text{H}_{\text{sat}}]$ and held constant on a temperature of 300 °C for max. 20 days. (Fig. 5). The effects of using fresh prepared, but not conditioned devices are clearly visualized (blue line). The unsatble phase here is indicated as “post preparation initiation phase” PPIP).

In oppsite to this, the influence of a well adjusted sensor conditioning step (step 8 in chapter 2.3) is clearly demonstrated: by this a constant EMF-phase is achieved already after lead-times of significantly less than 24 h (red line) in contrast to some days for unconditioned sensors. A narrow steady and continuous increase of the EMF also occurs, caused by slight losses of the hydrogen content (outgassing). Cooling down (test

cut-off) leads to falling voltages (melt becomes quickly saturated).

Some devices revealed insufficient functionality without any outer visible evidence. Post mortem analyses of those sensors showed, that obviously insulation of WE and RE by gas bubbles in the HCE annealing step (step 3) occurred. Suitable procedures (step 2) are convenient to avoid such hollows and voids within of the HCE.

Liquid lithium reveals a distinct adhesion to the niobium membrane surfaces. To deliberate the sensor heads after use, treatment (under argon atmosphere) with pure absolute ethanol and polishing with a woolen cloth were established as a convenient procedure. But prior to use of those refurbished devices, they carefully have to be conditioned again (steps 8 + 9, chapter 2.3).

In the early ECSLL-design phase, initially a distinct loss-rate of devices seemed to be highly probable due to chemical attacks in the harsh conditions (temperature + lithium + impurities). But those incidents did not occur in the suspected degree: the used Nb-heads did not show damages or traces of destructive influences caused by the Li-melt. Measurements also with temperatures > 300 °C for durations of several days showed no stronger impact on the sensor heads (and the sensor functionality). Therefore, the current ECHSLL layout has proven to be reliable and applicable.

4. Summary and outlook

For the first time an electrochemical sensor was designed and realized for detecting hydrogen impurities in liquid lithium. The sensor was designed for the use in the Impurity Control Systems of IFMIF-DONES. The demanding challenges, to elaborate suitable materials and their durable combination under the highly aggressive operating conditions in the liquid lithium melts, were successfully resolved. The membrane material was appointed by an intense research and H permeation calculations. Niobium revealed to be suitable and stable in the interactions with the lithium melts and also with the other chemical systems.

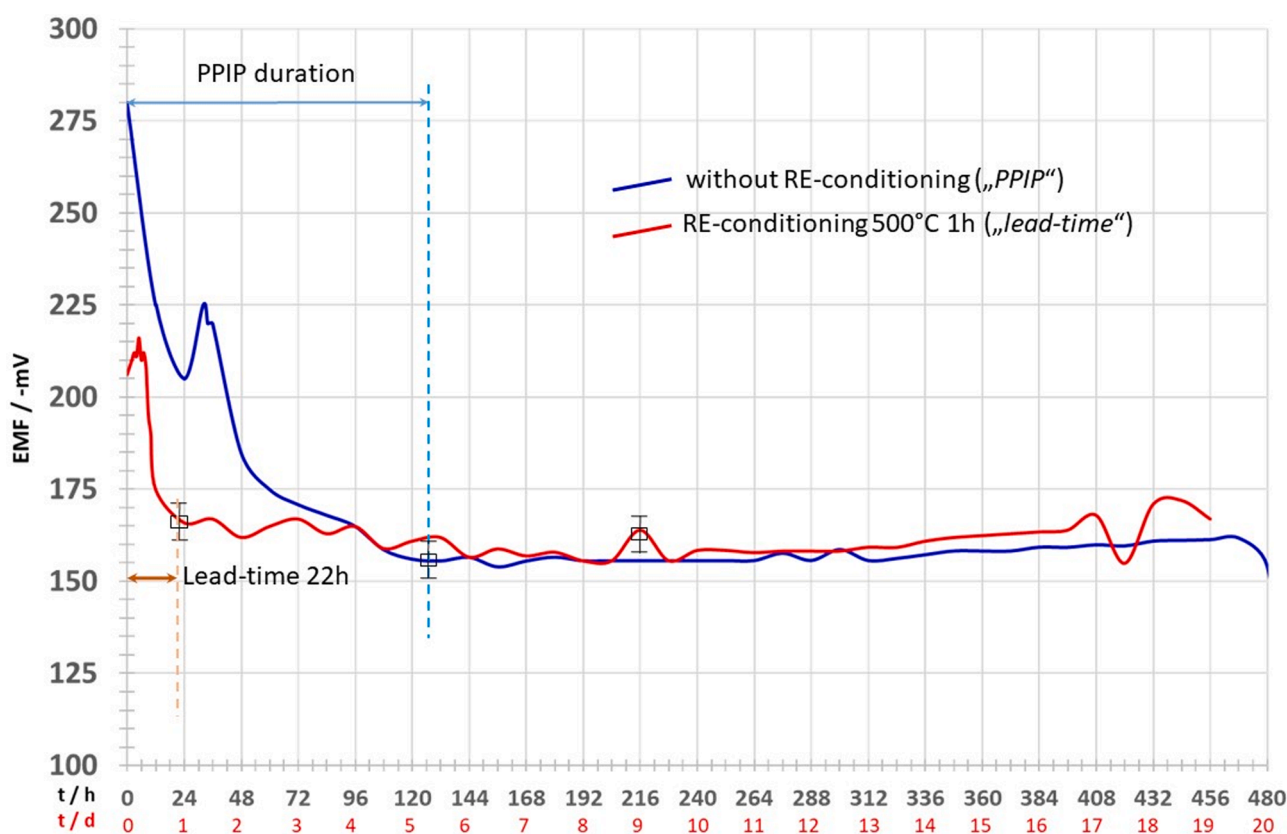


Fig. 5. long-time experiments of sensors in different initial conditions.

The performed tests showed that the sensors worked properly and indicate EMF values in good accordance with the adjusted hydrogen concentrations, so that valuable calibration curves could be elaborated, and confirmed, that reproducible measurements are possible over long-term application as required in IFMIF-DONES.

The temperature dependent analyses indicate, that the sensitivity increases with operation temperature. However, application conditions and temperature introduced degradation effects may limit the application temperature. Under electrochemical aspects 400 °C are seen as a good choice, whereas loop operation favors lower temperatures. Future sensor qualification has to define optimized working properties under such views.

The ECHSL device in its current design was initially designed to measure the total hydrogen (Q_2) content of IFMIF-DONES and to show the applicability of an EC-sensor in Li-melts; due to their identical electrochemical properties it is rather difficult to detect selectively the isotopes protium, deuterium and tritium at the moment. However varied concepts of ECHSL are conceivable (e.g., varied membranes and parallel measurements) might enable the wished differentiation of H-isotopes as discussed in [20] and will be future development goals, too.

As future improvements sensors with drastic thinner membranes of 0.4 down to 0.3 mm are to be manufactured in order to achieve quicker response times. After laboratory testing of the sensors in stagnant Li environment, qualification and calibration has to be performed in Li flow (loops). For this, reduction of the EC-electrode sizes is planned (diameters will be reduced down to 10–14 mm). Cycling of H concentration with different time constants has also to be included into the qualification measures.

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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