New developments of hydrogen impurity online-monitoring in liquid lithium of IFMIF-DONES

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ABSTRACT

On the way to future nuclear fusion power plants, the International Fusion Materials Irradiation Facility (IFMIF) – DEMO Oriented Neutron Source (DONES), is an important key element between ITER and DEMO to study before the influence of DEMO-neutron irradiation on foreseen fusion materials. The core of DONES, currently under construction near Granada, Spain, is based on a circuit containing liquid lithium at elevated temperatures acting as a functional material for the (d,n)-Li reaction in a materials test cell. In addition to this actual function of DONES, there are important aspects of maintenance in which hydrogen isotopes are generated under operating conditions and dissolved in this aggressive and very reactive alkali metal. This implies strong unfavourable effects on the applied structural materials, e.g. hydrogen embrittlement and others.

To counteract these unfavourable effects, endangering the safe operation, an Impurity Control System (ICS) is an integral part of the DONES instrumentation. As part of the tasks of the European Neutron Source (ENS) to develop redundant systems for monitoring impurities, a special sub-task was defined for the development of an electrochemical H-sensor for concentrations in liquid lithium, ECHSLL. It is determined by detecting the electrical potentials of the lithium melts compared to a standard Li-based chemical reference system. This allows an inherent material property to be directly correlated (i.e. through appropriate electrochemical instrumentation) with chemical concentration values. This article presents important advancements in the applied ECHSLL technique, such as improving laboratory measurements from stagnant conditions to dynamic and realistic flow conditions of the liquid lithium material, as well as appropriate approaches to overcome the challenges in distinguishing the hydrogen isotopes by ECHSLL system (protium and deuterium among given laboratory conditions).

1. Introduction

IFMIF-DONES is an approach to investigate materials properties under nuclear fusion conditions prior to their application in DEMO. DONES hereby is an EUROfusion coordinated approach of an such IFMIF neutron source, meanwhile under construction near Granada/Spain. Its main component is a Liquid-Lithium (LL) target, which produces a nuclear (d,n)-Li-reaction by deuteron bombardment. Generated by a 40 MeV ion beam, fusion-like neutron irradiation (14 MeV) then will undergo interaction relevant DEMO-material specimen in a test cell as shown in Fig. 1 [1].

Besides the huge challenges in engineering and handling the main nuclear physics for material investigation, also security issues are of highest, due to that DONES is a nuclear facility, which has to be in accordance with the statutory nuclear regulations. The Li-target is the key part within a loop containing about $14\,m^3$ of Liquid Lithium (LL). LL is an aggressive material sensible to impurities, hence one important issue is the enrichment of gaseous impurities. Due to the deuteron bombardment side-reaction and effects, an enrichment of hydrogen will occur (by all of its isotopes H,D,T).

This has a strong impact on all structural materials (tubes, tanks, containers, pumps, etc.) in contact with LL, inducing danger of fatal failures under operation by embrittlement and fatigue stresses. Due to its high chemical reactivity with several media (air, water, ceramics) and also potential flammability, its safe use and handling must be always guaranteed [2]. Especially steels that are otherwise stable in lithium lose this stability in the presence of gaseous impurities as hydrogen [3–5]. Knowledge of their concentrations is therefore essential. Besides several (partly costly and complex) possibilities, as diffusion-based mass-spectrography [6,7], one approach to control hydrogen impurities in the frame of a contemporary DONES-instrumentation is the development of ECHSLL, an electrochemical (EC) hydrogen sensor for LL [8,9].

Physical values (electric potentials) to be monitored are a direct consequence of the material properties and their relations (chemical values). Hence, the use of electrochemical effects is self-evident and a very practical instrumental approach. Although EC-sensors are widely used sensor systems in aqueous chemistry(for determination of H-species), established application in liquid metal systems however is limited to a drastically smaller extent, as Na, Pb-Bi, Pb-Li, due material compatibilities and different practical problems [10–12].
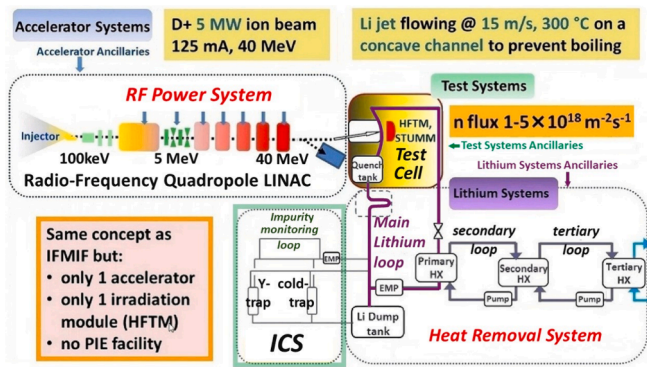
Fig. 1. Principal flow diagram of DONES with the central main Li-loop. ICS indicates the Impurity Control System where in its loop the H-monitoring by ECHSLL will be installed [1].

2. Experimental

The development of an *Electrochemical H-Sensor for Liquid Lithium* (ECHSLL) revealed to be a huge challenge. The given limitations in material availability, compatibility, manufacturing aspects and maintenance, leaded to the present applied design (Fig. 2a), using niobium membranes and hydrogen conducting electrolytes. The main functionality is to oppose two Li-H melts, from which one is an all-over stable reference, and the other the investigated specimen, resulting in the formation of a potential difference (Fig. 2). This voltage E is defined by the

$$Nernst - equation \quad E = -RT/nF \ln\left([H]_{dissolved}/[H]_{reference}\right) \quad (1)$$

with R = universal gas constant 8,3144 J/K•mol, T = melt temperature in K, n = number of electrons transferred in the EC reaction (1 for hydrogen), F = Faraday constant, $[H]_{diss}$ = mole fraction of H in the investigated Li-melt.

$[H]_{ref}$ is mole fraction of saturated H in the reference Li-system (constant for given temperature and "supersaturated" by an high excess of Li. Under operating conditions, the striking point is $[H]_{diss}$ being then the only unknown quantity. Following arrangement shows all materials interacting in the ECHSLL cell.

Li-H melt // Nb // CalCl$_2$ + CaH$_2$ // Nb // Li + LiH (eq.).

Fig. 2(a) shows the principal cell design and functionalities therein, Fig. 2(b) partly and fully manufactured sensors, WE and RE.

The sensor system is designed to act as single-rod measuring cell SMRC made of double-tubed niobium membrane heads as the EC potential generating parts. The inner tube contains the reference Li-H-melt as reference electrode, embedded in an hydride conductor electrolyte (HCE) made of 5 at-% CaH$_2$ in CaCl$_2$ (further technical and chemical details of ECHSLL see [8,9]), filled in the outer niobium tube/head (working electrode WE). Current ECHSLL geometries are: length 250
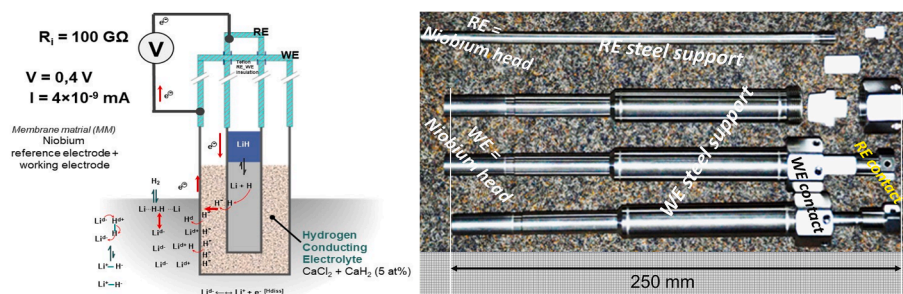
mm, outer niobium head diameter 14 mm, niobium thickness 400 μm (thickness will be reduced when thinner membrane become available). The applied SMRC design spares any outer counter and auxiliary electrodes (as Haber-Luggin-capillary), and avoids any distortions caused by systematically undefined WE-RE distances and strengthen comparability of different experiments and sensor devices.

In its currently applied laboratory set-up, the sensors are combined with the EC multiple-device IVIUM-Vortex EIS-Multiplex. Three independent Li-melts can be investigated simultaneously, applying different EC techniques, various parameters, and/or time schedules (Fig. 3).

2.1. Experimental approach for isotope measurements

Isotopes hardly can discriminated and distinguished within one unique measurement because EC standard potentials do not change with the atom mass. However, formation of "electrochemical potentials" (i.e. electric potentials as result of the chemical conditions) of is a result of mole fractions resp. concentrations and/or their basic standard potentials, as it is formulated by the Nernst law. But effects on EC measurements as result of physical conditions. Literature research confirm possible approaches to distinguish isotopes via detour resp. indirect methods as the Gorski-effect [13], due to the different weights of isotopes having an impact on diffusion and also permeability constants [14,15]. Hence, under certain conditions a use of the difference in the formation of potential differences will be possible (a well known example is the directed enrichment of heavy water in conventional water electrolysis [16]). But the electrochemical expertise shows, that such isotope-discriminating does not belong to established EC techniques, consequently is applied scarcely due of the complex multiple efforts (and this up-to-date only exclusively in aqueous systems).

As described by Bigeleisen et al. [17,18], a series of comparing experiments with a replacement of one species by one of its isotopes will show, different effects enabling a distinguishing method. Adopted to the ECHSLL system, this means a series of relevant constellations as shown in Fig. 4. With a replacements of the protium-carrier lithium hydride LiH) by lithium deuteride LiD in RE and WE in all the different experimental conditions, there are four possible H-D variations: standard hydrogen sensor EC**H**SLL vs. Li-H melts and Li-D, and EC**D**SLL (=ECHSLL with RE LiD-Li) vs. Li-H melts and Li-D melts.

This counts principally in the same way also for tritium (³H). Tritium exchange would show bigger effects due to its bigger mass, but due to its radioactivity, tritium-handling can be carried out only in special tritium laboratories.

3. Applying ECHSLL with defined flow-rates

A further approach to investigate electrochemical properties of lithium materials under laboratory conditions with limitations as stagnant melts is being the R&D of a rotating electrode system. This would enable a controlled flow regime of the ECHSLL versus the Li-melt also in existing stationary laboratory set-ups.
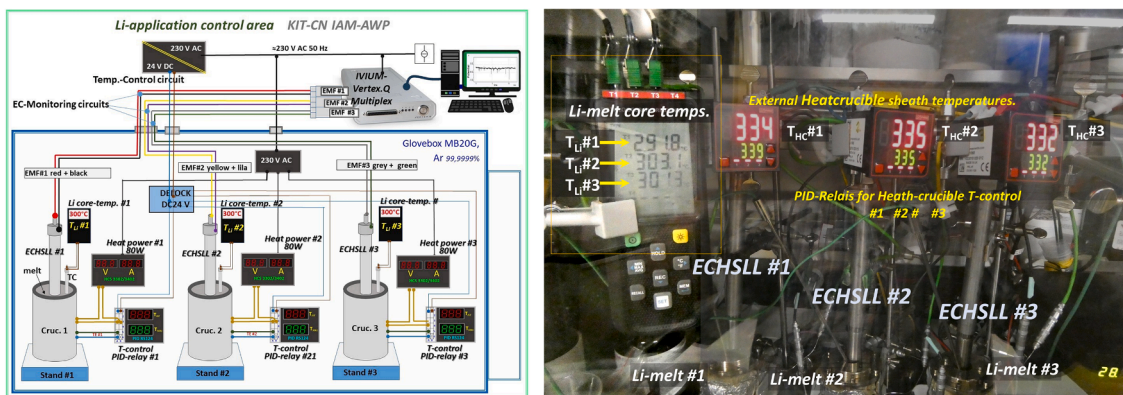

Fig 2. A) echsll scheme showing el.chem. function and definition of working electrode we and reference electrode re. b) sensor devices and single components as we, re contact sites and insulations (teflon), niobium sensor heads 14 mm diameter, support structure 20 mm diameter.

Fig 3. a) flow-diagram of electric circuits for simultaneous three ECHSLL-measurements b) applied test stand array working at Li-melt core temperatures T = 300 °C (occasionally possible max. 600 °C for conditioning etc.).
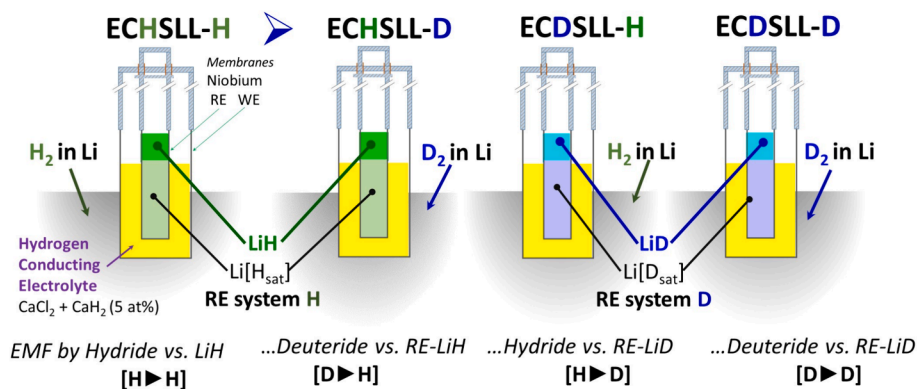

Fig 4. Approach of comparing EMF measurements applying replacement of protium (H) by deuterium (D) in Li- melts and RE systems in the 4 possible variants with protium.

3.1. Rotating electrode basics

In analytical electrochemistry, rotating disk electrodes (RDE) are applied in hydrodynamic voltammetry. Those rotating WE are used in electrochemical studies for different chemical phenomena, but up-to-date exclusively only in aqueous and related low-temperature systems [19,20].

At a turning RDE surface, the investigated liquid material is dragged by the spinning disk and due to centrifugal forces the liquid material is flowing perpendicular in z-direction and being flinged away in horizontal x,y-direction from the sensor-head surface. The result is a laminar flow of towards and across the electrode. The convective flow-rate is then dependent of the RDE rotation speed ω in the Levich equation < 2> (Fig. 5a). This is a fundamental contrast to stagnant experiments, where steady-state conditions are strongly limited by diffusion. As consequence, under rotating conditions the monitored currents are typically

much higher than under stagnant conditions (ω = 0); with the rotator turned off, the rotating electrode than acts as stationary electrode and allows a direct comparison to stagnant conditions under identical set-up conditions.

$$Levich - equation : I_L = 0,62 \, n \, D^{2/3} \, F \, a \, \nu^{-1/6} \, \omega^{1/2} \, c \qquad (2)$$

with n = number of moles of electrons transferred in the EC half reaction (1 for hydrogen), F = Faraday constant (C/mol), a = electrode area (cm^2), D = diffusion constant (cm^2/s), ω = angular rotation rate (rad/s), ν = kinematic viscosity (cm^2/s), c = analyte concentration (mol/cm^3).

3.2. Rotating electrode design for liquid lithium

The Levich-equation counts in principle only for the flow at the circular WE surface level ("Levich-horizon"), therefore the Li-melt flow must not reach the side walls. Alternatively, if being penetrated in LL, in
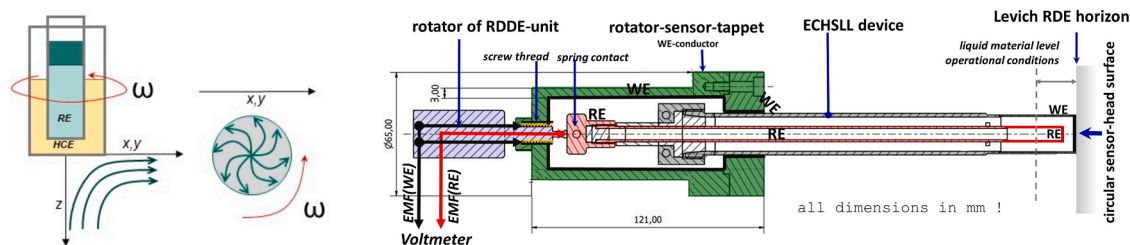

Fig 5. a) left:: hydrodynamics at a rotating electrode surface (side and lateral view; b) right: construction drawing of RLE showing rotator (light-blue), tappet (green) and sensor (grey); contacts are indicated black for WE lines and red for RE (here RLE in horizontal view!).

this case, the Levich-current by $< 2 >$ increases by a particular depth-dependent factor A, to be determined for the experiment: IL' = A•IL.

In any case, in contrast to the Nernst equation $< 1 >$, which defines a detected signal (voltage) as consequence of a chemical parameter, the Levich equation $< 2 >$ defines a signal (current) as consequence of physical parameters.

Literature research revealed, that application of rotating WE systems with liquid metals, and especially intended use in LL, meets some obstacles, therefore scarcely had been described [21,22]. Nevertheless, RDE conditions are more transferable and comparable to DONES loop flow conditions than diffusion controlled stagnant conditions.

The approach for a rotating system in LL (provisional working title used here *Rotating Lithium Electrode* RLE) is based on a RDE with two insulated contact sides. (Rotating Ring-Disc-electrode RDDE, IPS Elektroniklabor, Eppertshausen/Germany): the central RDDE contact is connected directly to the RE head contact of the ECHSLL, whereas the rotator of the outer ring contact (screw thread) was bound to the sensor WE by a specially manufactured sensor-rotator tappet (SRT).

Fig. 5b shows the engineering detail drawing (cross section) of the first RLE prototype: blue area indicates the original RDDE rotator unit (to be fixed by an external frame), from which the central spring RDDE contact (indicated red) connects the ECHSLL-RE with the voltmeter device. The tappet (indicated green) supports mechanically and electrically the WE-contact sites via rotating screw thread and large area-enclosure (black lined)

Measurements of currents by the ECHSLL-device are enabled by the high-sensitive IVIUM-Potentiostate system detecting currents in micro- and nano-ampères. Furthermore, any existing measurement set-ups under stagnant/stationary conditions, could be upgraded by this new RLE technique to controlled flow regimes to determine physical parameters by $< 2 >$ as viscosity, diffusion constant and at least also concentrations.

4. Summary and outlook

An electrochemical sensor is being designed and constructed for detecting hydrogen impurities in liquid lithium of IFMIF-DONES. The demanding challenges to elaborate further and more sophisticated developments under the highly aggressive operating conditions in the liquid lithium melt successfully were resolved.

Because those sensors initially had been designed for the measurement of general hydrogen contents ("Q_2"), a selective 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.) and the realization in an adopted multiple experimental test stand seem to be a promising approach for the design of a EC(P,D,T)SLL sensor.

To overcome the issue of measurements in stagnant Li-melts compared to lithium material flow in loops and flowing systems, a new electrode device for liquid lithium was developed enabling also forced convection of liquid metal dynamics in given stagnant laboratory systems, and principally also could be used in existing Li-melt flow systems for special investigations.

CRediT authorship contribution statement

Nils Holstein: Writing – original draft, Visualization, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Wolfgang Krauss:** Writing – review & editing, Validation, Supervision, Resources, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Jürgen Konys:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Francesco Saverio Nitti:** Writing – review & editing, Validation, Supervision, Project administration,

Funding acquisition, Formal analysis.

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.

Data availability

Data will be made available on request.

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