Oxygen partial pressure control for microgravity experiments

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A system consisting of a high-temperature yttrium-stabilized zirconia (YSZ) based oxygen ion pump and potentiometric sensor enables precise measurement and control of oxygen partial pressure, \( p_O_2 \), at elevated temperatures within 0.2 to \( 10^{-24} \) bar. The principle of operation as well as the influence of temperature and gas buffers like \( H_2/H_2O \) on the \( p_O_2 \) is discussed. The ion pump is controlled by a microcontroller system and adjusts the oxygen partial pressure with an uncertainty of \( \Delta \log(p_O_2/\text{bar}) < 0.02 \) and response times between 5 and 90 s over the entire \( p_O_2 \) range. The oxygen ion pump is tested in combination with the electromagnetic levitation. Here, the surface tension of molten Ni at 1720 °C as a function of oxygen partial pressure is determined. A good agreement of this measurement with calculated value confirms the applicability of the system for high-temperature measurement and control of \( p_O_2 \). The developed hardware is suitable for the electromagnetic levitation facility onboard the international space station (ISS).

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1. Introduction

The investigation of the material properties in the liquid phase at elevated temperatures requires often precise knowledge of the oxygen partial pressure. Surface oxidation and oxygen dissolution may affect the properties significantly. Depending on the considered substance, its oxidation may occur even at extremely low \( p_O_2 \), such as \( 10^{-24} \) bar. Therefore, it is required to control the \( p_O_2 \), with range depending on the specific experiment.

Measurement of \( O_2 \) concentration at elevated temperatures using e.g. optical or photoacoustic methods is not applicable for systems, where oxidation at elevated temperatures takes place at very low \( p_O_2 \). The sensitivity of such devices is hardly better than \( 10^{-6} \) bar. Further, the information about the oxygen content does not necessarily correspond to the oxygen activity which is the property of interest. Also, resistive and amperometric methods offer either a narrow range of measurement or a sensitivity only of about \( 10^{-7} \) bar, respectively. Therefore, potentiometric systems are most favorable. They allow measurements of the \( p_O_2 \) in the range from \( 10^9 \) to \( 10^{-24} \) bar and exhibit very short response times.

Control of oxygen partial pressure in such wide range is not possible using conventional gas mixing systems. Gas buffers, like \( H_2/H_2O \) and \( CO/CO2 \), enable relatively precise adjustment of \( p_O_2 \) below \( 10^{-15} \) bar. The oxygen partial pressures above \( 10^{-7} \) bar may be obtained using cascades of conventional mass flow controllers. Around the equilibrium composition, where stoichiometric amounts of gases are reacting, smallest fluctuations in gas composition shift the \( p_O_2 \) by several orders of magnitude. In order to overcome this difficulty, an oxygen ion pump based on yttrium-stabilized zirconia (YSZ) is applied. In contrast to conventional mass flow controllers which adjust the oxygen flow with an uncertainty of about 50 mm³/min, the oxygen ion pump can control oxygen flow with a resolution of at least 0.001 mm³/min. In combination with a potentiometric sensor, it enables precise transport of oxygen into and out of the system and thus allows precise control of the \( p_O_2 \) within the \( 10^{-24} \) to 0.2 bar range.

One of the applications, where oxygen partial pressure must be known, is the determination of the surface tension of liquid metals and alloys at elevated temperatures. Even under high-purity conditions, undefined atmospheres may lead to oxidation of the samples which impacts the surface tension by 10 to 30%. Depending on the sample, the oxygen partial pressure has to be below \( 10^{-24} \) bar to avoid oxidation.

As the contact based techniques, such as sessile drop technique [1–4], can often lead to erroneous results, in particular due to chemical reactions between the sample and the substrate, contactless techniques such as the electromagnetic levitation are indicated for investigation of high-purity materials. Here, a molten sample is levitating in an electromagnetic field, giving an oscillating drop [5]. Even though the oscillations are influenced by the environment, like gas perturbations in the vicinity of the sample or drop rotations, mathematical treatment is developed which enables extraction of the surface tension from this data [6]. Since any contact between sample and crucible is avoided with this technique, it is a highly...
suited approach for determination of material data for high-purity materials. In order to reduce the perturbations introduced by strong electromagnetic field as required to levitate the sample under 1 g, the conduction of this experiments in microgravity conditions on-board the international space station (ISS) is mostly favorable.

2. Operation principle

2.1. Oxygen ion pump

The oxygen ion pump is based on an ionic conductor operated at a temperature sufficiently high to enable the transport of $O^{2-}$ through an electrolyte, but low enough to suppress the electronic conduction. In case of dominant ionic conductivity, the flux of oxygen is defined as [7–9]:

$$J_0 = \frac{I}{F},$$

where $I$ and $F$ correspond to the electric current and Faraday constant, respectively. Using a pumping current of 40 mA a transfer of about 8 cm$^3$ O$_2$ per hour occurs. If the oxygen flow $J_{O_2}$ is low with respect to the total gas flow, the resulting oxygen partial pressure depends on the total pressure $p_{tot}$, total gas flow $J_{tot}$ and the initial oxygen partial pressure in the carrier gas $p_{O_2}^0$:

$$p_{O_2} = p_{O_2}^0 + p_{tot} \frac{J_{O_2}}{J_{tot}}.$$  (2)

The scheme of the oxygen ion pump is shown in Fig. 1 and explained in detail in Section 3.1. Here, the large electrode is used to transport oxygen from the reference gas (ambient air) to the carrier gas. The small electrode is used to monitor the electromotive force which is given by the Nernst equation

$$E_{cell} = \frac{RT}{4F} \ln \left( \frac{p_{O_2}}{p_{O_2}^0} \right),$$

where $R$ and $T$ are the universal gas constant and the temperature, respectively. The oxygen partial pressure in the reference gas, $p_{O_2}^0$, equals 0.209 bar. The error introduced by regarding this value as constant is negligible.

2.2. Oxygen equilibrium in buffer gas mixtures

In case of the presence of buffer gas mixtures, Eq. (2) describing oxygen partial pressure does not apply. Here, the gas equilibrium constant is negligible.

2.3. Correction of the oxygen partial pressure

If the temperature of the sample differs from the operating temperature of the oxygen sensor, the $p_{O_2}$ must be corrected. The

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O,$$

with the equilibrium constant

$$K(T) = \frac{\left(p_{O_2}^0 + \Delta p_{O_2}\right)}{\left(p_{H_2}^0 + \Delta p_{H_2}\right)\left(p_{O_2}^0 + \Delta p_{O_2}\right)^{1/2}}.$$  (5)

Here, $p_{O_2}^0$, $p_{H_2}^0$ and $p_{O_2}^0$ correspond to the initial partial pressures of hydrogen, water vapor and oxygen, respectively, before the reaction takes place. The temperature dependent equilibrium constant is defined as [10]:

$$K(T) = 1.423 \cdot 10^{-3} \exp \left( \frac{2.56 eV}{k_B T} \right).$$  (6)

Combining Eqs. (1), (2), (5) and (6), the oxygen partial pressure adjusted by an oxygen ion pump $p_{O_2} = p_{O_2}^0 + \Delta p_{O_2}$ is calculated numerically for given initial partial pressures and temperatures and shown in Fig. 2. As carrier gas, Ar (99.999%, $p_{O_2} = 1.6 \cdot 10^{-8}$ bar) mixed with H$_2$ ($p_{H_2} = 0.005$ bar) flowing at 20 cm$^3$/min is used.

Based on Fig. 2 three different regions are discussed:

- **Low $p_{O_2}$ region.** Hydrogen and nearly all oxygen form water vapor resulting in $p_{O_2}$ as low as $10^{-25}$ bar at 600 °C and a pumping current $I \approx 0$ mA (see Fig. 2). Due to very high excess of H$_2$, further titration of oxygen ($I \approx 8$ mA) results in slight increase of oxygen partial pressure.

- **Stoichiometric point.** Here, a nearly stoichiometric composition of H$_2$ and O$_2$ to form water is reached. Only very slight changes in the pumping current ($I \approx 8$ mA) and thus in the amount of oxygen provided, result in $p_{O_2}$ changing by several orders of magnitude.

- **High $p_{O_2}$ region.** Nearly all hydrogen reacts with oxygen and forms water vapor. Further introduction of oxygen into the system ($I \approx 9$ mA) leads to a slight shift of equilibrium and to a steady increase of oxygen partial pressure, only. The control of $p_{O_2}$ using conventional gas mixing systems is feasible.

The amount of electric current applied to the oxygen ion pump causing a change of $p_{O_2}$ by one order of magnitude at the stoichiometric point is shown in Fig. 3. As shown there, at low flow and low temperatures, the pumping current has to be controlled precisely in a range of $10^{-8}$ A. If such expectation cannot be fulfilled, either higher temperature or, according to Eq. (2), higher flow rates are required.

2.3. Correction of the oxygen partial pressure

If the temperature of the sample differs from the operating temperature of the oxygen sensor, the $p_{O_2}$ must be corrected. The
order of magnitude calculated for different temperatures and total gas flow.

A certain partial pressure of oxygen, hydrogen and water are added to \( p_{O_2} \) and \( p_{H_2} \), respectively. For further discussions, the amounts of hydrogen and oxygen bound in water are added to \( p_{H_2} \) and \( p_{O_2} \), respectively. The approach is used to define a reference gas composition and to calculate subsequently the partial pressures of oxygen, hydrogen and water after completing the reaction according to Eq. (4) as a function of temperature. Those properties are denoted again by \( p_{O_2} \), \( p_{H_2} \), and \( p_{H_2O} \), respectively. Similar considerations can be done for gas mixtures containing \( O_2, CO \) and \( CO_2 \). However, the following application examples base on atmospheres which contain very little amounts of \( CO \) and \( CO_2 \) with respect to \( H_2 \) and \( H_2O \). Therefore, the occurrence of carbon containing gases is ignored for the further discussion.

The gases used for experiments contain a fixed amount of hydrogen \( p_{H_2} \). The amount of oxygen \( p_{O_2} \) required to adjust a certain \( p_{O_2} \), is provided by an oxygen pump. As explained in more detail in Section 3, two cases are realized:

1. Intentional insertion of 0.5% \( H_2/Ar \) gas flowing through the oxygen pump at rate of 20 cm\(^3\)/min.

In order to calculate the temperature dependence of the \( p_{O_2} \), Eq. (5) is solved for \( p_{O_2} = p_{O_2}^{0} + \Delta p_{O_2} \). In a first step \( p_{O_2} \) is varied until a certain \( p_{O_2} = p_{O_2}^{0} \) at 600 °C, i.e. at the sensor temperature, is adjusted. In a second step, the temperature is varied using fixed values for \( p_{H_2} \) and \( p_{O_2} \).

Fig. 4 shows the result for \( p_{O_2}^{0} = 10^{-7} \) bar and different \( p_{H_2}^{0} \). It becomes obvious that changes in temperature have a minor impact on the \( p_{O_2} \) as long as \( p_{H_2}^{0} \geq 10^{-7} \) bar. Below that value there is a strong temperature dependence which must be regarded while discussing experiments where the temperature of the oxygen sensor and the sample are different.

It should be noted that the \( p_{O_2} \), below which corrections are necessary strongly depends on the \( p_{H_2} \). Higher total hydrogen concentrations shift this \( p_{O_2} \) to higher values.

3. Experimental

The oxygen loading system (OLS) consisting of ion pump, potentiometric sensor and mechanical gas circulation pump is tested in two different environments. Laboratory conditions, free of strong electromagnetic fields and dust particles in carrier gas due to evaporation of liquid samples, enable precise determination of oxygen pump’s performance, response time and signal stability. In case of the experiments, where the oxygen partial pressure is adjusted during levitation, strong electromagnetic fields impact potentially the stability of the control system. The experimental results are correlated with theoretical considerations on surface tension as a function of oxygen partial pressure.

3.1. Oxygen control system

The \( p_{O_2} \) is controlled using two YSZ tubes which are operated as oxygen pump and sensor, respectively. The approach enables to measure the \( p_{O_2} \) independent of the pump at positions in the experimental setup which are defined by the actual application. In general, the sensor should be installed in the close vicinity of the sample to be investigated. It must be noted, that the pump is equipped with an additional oxygen sensor whose signal is used to improve the stability of the control algorithm.

The one-side closed, 8 mol% \( Y_{2}O_{3} \)-doped \( ZrO_{2} \) tubes with platinum electrodes are purchased at Metrotec GmbH, Kirchheim, Germany. The scheme and the dimensions of the first tube used primarily as oxygen pump are shown in Fig. 1. Since the device is also designed to measure the \( p_{O_2} \), the outer face is covered with platinum paste in two regions, i.e. there is a large pumping area of about 125 cm\(^2\) and a small sensor area of about 3 cm\(^2\). Due to the large distance between the pumping and sensor electrode, no impact of the pumping current on the Nernst potential is observed. The inner face is coated with a common platinum electrode. The second tube is operated as oxygen sensor. The device is coated with a small outer electrode of 3 cm\(^2\) and a large inner electrode. The general design corresponds to that of the oxygen pump.

Both, the oxygen ion pump and the sensor are operated at 600 °C. This temperature ensures sufficiently high oxygen ion mobility and long-term stability of the system. The YSZ tubes are enclosed in...
large thermal insulation blocks to minimize the temperature gradients. It should be noted that the temperature is monitored very close to the oxygen sensors. The temperature of those small areas is expected to be very uniform and is used to calculate the $p_{O_2}$ according to Eq. (3). Potential temperature fluctuations in the larger pumping area do not impact the $p_{O_2}$ control since the applied electrical current is the property of interest.

Since the system is operated in an environment, where strong electromagnetic noise occurs, commercial temperature controllers do not fulfill the stability requirements under such conditions. Therefore, a robust custom device is built. In order to reduce the crossfeed between the power supply and monitored temperature, commonly used thermocouples are replaced with resistive temperature sensors. Further, EMI shielding for control electronics and for entire OLS is provided.

The pumping current $I$ of at most 40 mA is adjusted by a pulse width modulation control based on a PID algorithm. Thereby the polarity of the current can be changed. The controller achieves a resolution of about 1 μA.

Because of a strong nonlinearity of the $p_{O_2}(I)$ curve (see Fig. 2), classical PID algorithm cannot be used. The necessary modifications include i.a. dynamic adjustment of PID parameters at different oxygen partial pressures. Additionally, the system features a cascade PID controller, which enables $p_{O_2}$ adjustment at two different potentiometric sensors.

### 3.2. Levitation facility

In order to confirm the applicability of the oxygen control system for electromagnetic levitation experiments, it is integrated at the levitation facility. The entire system is mounted on top of the experimental chamber (EC). The carrier gas with oxygen content adjusted by the pump is directed to the sample, whereas an additional potentiometric sensor monitors the oxygen partial pressure in gas leaving the EC.

### 4. Results and discussion

#### 4.1. Control of oxygen partial pressure in buffer gases

The performance of the oxygen ion pump using the aforementioned 0.5% H₂/Ar buffer gas is shown in Fig. 5. Here, the oxygen partial pressure is adjusted stepwise between $10^{-3}$ and $10^{-20}$ bar over several days. Throughout all oxygen partial pressures a signal stability of $\Delta \log(p_{O_2}/\text{bar}) < 0.02$ is achieved.

![Fig. 5. Oxygen partial pressure regulated stepwise between $10^{-7}$ and $10^{-20}$ bar in a 0.5% H₂/Ar at 600 °C.](image)

#### 4.2. Control of oxygen partial pressure without buffer gases

The result of oxygen ion pump controlling $p_{O_2}$ at the nominally buffer-free carrier gas (Ar 99.999%) is shown in Fig. 6. Here, the oxygen partial pressure is varied stepwise between $10^{-7}$ and $10^{-3}$ bar. Remarkable is the very short response time of less than 90 s and signal stability of $\Delta \log(p_{O_2}/\text{bar}) < 0.02$. Since the oxygen control system features switching of the pumping current polarity, it is possible to control $p_{O_2}$ below and above oxygen's partial pressure in the carrier gas.

#### 4.3. Application example

Several pure metal samples are melted in the levitation facility at different oxygen partial pressures. At the same time the oscillations of the surfaces are observed with a high-speed camera. Based on this data, a $p_{O_2}$-dependent surface tension is determined [11]. According to theoretical considerations, in case of dilute solution of oxygen in a liquid metal, the surface tension $\gamma$ is expressed by the Belton equation [12]:

$$\gamma = \gamma^{\text{pure}} - RT \ln(1 + Ka).$$

where $\gamma^{\text{pure}}$, $R$ and $T$ are the surface tension of pure liquid, universal gas constant and temperature, respectively. $\Gamma$, $\gamma$, $K$ and $a$ are the surface excess coefficient, adsorption coefficient and bulk activity of oxygen, respectively.

Exemplarily, a result of these tests is shown in Fig. 7. Here, a 99.999% Ni sample is molten and levitated at 1720 °C. An Ar gas (99.9999%) with adjusted $p_{O_2}$ at flow rate of about 7000 cm³/min is supplied directly at the sample. Major residual components of the Ar used are hydrogen and water ($p_{H_2} < 0.5$ ppm, $p_{H_2O} < 0.5$ ppm). For the following discussion a totality $p_{O_2} = 10^{-7}$ bar is assumed. Taking the related results from Fig. 4, a scale for the $p_{O_2}$ at 1720 °C is generated and added to Fig. 7. Again, the influence of temperature on $p_{O_2}$ above $10^{-7}$ bar is negligible. As a consequence, no correction of the $p_{O_2}$ is required in the range, where the surface tension undergoes its major changes. Below that $p_{O_2}$, of course, corrected values at 1720 °C have to be considered.

The measured oxygen partial pressure dependent surface tension is compared with the value calculated with Eq. (7) and the previous measurement of pure Ni annealed at the same temperature in nominally oxygen-free atmosphere [11]. The experimental result shows a good agreement with the Belton equation. A slightly lower surface tension compared to the previous measurement may be a result of a statistical error.
5. Conclusions

A standalone system for oxygen partial pressure measurement and control is developed. It controls the $p_{O_2}$ within $0.2$ to $10^{-20}$ bar range with an uncertainty of $\Delta \log(p_{O_2}/\text{bar}) < 0.02$. The response time of the system is determined predominantly by the total volume of the experimental chamber. The developed hardware and electronics are thereby principally suited for later implementation into the EML (Electro-Magnetic-Levitator) facility onboard the ISS.

The system is successfully tested in the vicinity of high-power sources of electromagnetic fields, like e.g. power supply for the electromagnetic levitation facility. The surface tension of molten Ni determined as a function of oxygen partial pressure shows a good agreement with the Belton Equation. It confirms the correct operation of OLS set-up as well as the impact of $p_{O_2}$ on the metal's surface properties at elevated temperatures. The test series have revealed that the developed OLS can be employed and successfully operated even under the harsh environmental conditions of a high-temperature levitation facility.

Since the temperature of the sample differs from the operating temperature of the oxygen sensor, the $p_{O_2}$ must be potentially corrected. For the conditions here, no correction of the $p_{O_2}$ is required in the range above $p_{O_2}^{600} \approx 10^{-7}$ bar, where the surface tension undergoes its major changes. Below that $p_{O_2}$ corrected values at $1720 \degree C$ have to be considered.

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Fig. 7. The surface tension $\gamma$ of 99.999% Ni as a function of $p_{O_2}$. The dotted line corresponds to the previous measurement in nominally oxygen-free atmosphere [11] whereas the gray line corresponds to the Belton Eq. (7). A good agreement of the measurement with the calculated curve is clearly visible.