Molten salt electrolysis of Titanium using a TiO_2-C composite anode in halide electrolytes

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ABSTRACT

At RWTH Aachen University, Germany investigations are ongoing in order to develop molten salt electrolysis of titanium using a TiO_2/C composite powder anode. The main idea of the innovative process is based on the following principle. In a titanium halide (Hal) enriched and halide based electrolyte, $TiHal_x$ dissociates into Ti^{x+} and $xHal^-$ at a defined potential (current density). Subsequently Ti^{x+} is deposited at the cathode and Hal-atoms form at the anode. In "statu nascendi" these Hal-atoms react with the composite anode consisting of TiO_2 and C. $TiHal_x$ is formed again, which is dissolved in the electrolyte and a CO/CO_2-mixture leaves the anode compartment.

The paper will show that only iodide based electrolytes are suitable for this process and that the anode composition is dependent on the working temperature.

INTRODUCTION

For more than sixty years titanium is industrially produced by the Kroll process, which has a couple of disadvantages like low efficiency, high cost, batch wise operation, high energy consumption, complicated process control and a batch period of up to six days. Even Kroll thought his process would be substituted within a few years but until now no alternative has been successful introduced in industry. However the increasing demand for Titanium currently and in the future leads to a market pressure for a cheaper and high productive process. Since all commercial light metals are produced by molten salt electrolysis due to their ignoble character this seems to be a promising way for the production of titanium as well. Hence there are different electrochemical approaches being tested in the past and at the moment, but none of them has reached full production state until now.

INVENTION OF THE IME PROCESS

At IME Process Metallurgy and Metal Recycling - Department and Chair of RWTH Aachen University - experimental research is ongoing based on the idea to support the international research on molten salt electrolysis of titanium by developing an in-situ halidation step of TiO_2. [1]. This reaction shall take place in the same reactor and simultaneous to a $TiHal_x$-reduction at temperatures below 600 °C. The project is part of the Helmholtz Young Investigators Group "Electrolytic Production Routes for Titanium Matrix Composites" in cooperation with the German Aerospace Centre DLR in Cologne. The main tasks within this project are:

- Design of a suitable electrolysis setup
- Development of a composite anode
- Selection and testing of electrolytes
- Evaluation of process parameters

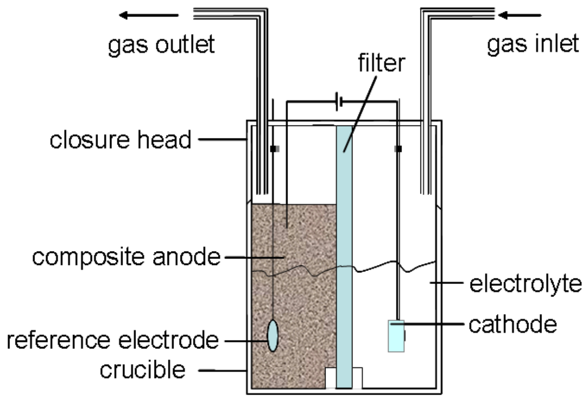

Figure 1: General cell design

Figure 1 shows the general cell design of the proposed process which is based on the following principle: In a titanium halide enriched and halide based electrolyte, TiHal dissociates into Ti^{x+} and $xHal^-$ at an adjusted potential (1). Ti^{x+} is deposited at the cathode following the sequence described by (2) and Halide-atoms form at the anode. In "statu nascendi" the Halide-atoms react chemically with the components of a composite anode, which is the main invention of the process presented here. The anode consists of TiO_2 and carbon and forms CO/CO_2 as well as $TiHal_x$ (2) which is dissolved in the electrolyte.

$$TiHal \rightarrow Ti^{x+} + 2Hal \qquad (1)$$

$$Ti^{4+} + e^- \rightarrow Ti^{3+} + e^- \rightarrow Ti^{2+} + 2e^- \rightarrow Ti \qquad (2)$$

$$TiO_2 + 2C + xHal \rightarrow TiHal_x + 2CO/CO_2 \qquad (3)$$

The different valence states of Titanium likely being present in the electrolyte pose an enormous challenge due to the chemical reactions (4) and (5).

$$Ti + 3Ti^{4+} = 4Ti^{3+} \quad (4)$$

$$Ti + Ti^{4+} = 2Ti^{2+} \quad (5)$$

As can be seen, four valent titanium ions tend to dissolve metallic titanium and interfere with the aimed process. Therefore Ti^{4+} should be avoided within the electrolyte in order to maintain a sufficient current efficiency. But using a composite anode consisting of TiO_2 and C the feed valence state of titanium is already four and at temperatures below 600°C no reduction with C takes place, so most probably all titanium dissolving from this anode is four valent. According to literature however [2], [3], a process window might be present to dissolve titanium with lower valence from this anodes.

EXPERIMENTAL WORK

Experimental Setup

The first challenge designing the experimental setup is to find a suitable crucible material, due to the fact that $TiCl_2$ (which will be present in every electrolyte as titanium source) will react with all kinds of oxide based materials. Metallic or carbon crucibles also can not be used for this investigation because of the contact between the powder anode and the crucible. As a result, every electric conductive material might take part in the electrolysis causing uncontrolled reactions.

As a consequence different nitride based materials were tested showing that BN and AlN were stable for at least a couple of days. However it turned out, that crucibles made from hexagonal BN were not mechanically stable during the solidification process causing problems to remove the electrolyte. Hence an AlN crucible was designed and built as shown in Figure 2. This crucible is used within a closed cell made from steel. The water cooled lid has airtight fittings allowing for electrical connection, temperature measurement, insertion of reference electrodes and sampling. (Figure 2)

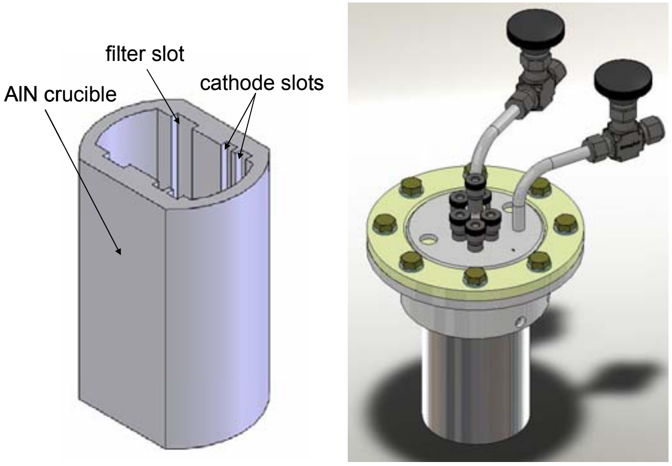

Figure 2: Designed AlN-crucible (left) and cell (right)

The cell itself is prepared in an argon filled glove box preventing contamination of water and/or oxygen .During the hole trial the cell is constantly flushed with argon and the off gas was passed into a washing bottle, collecting the salt components within the off gas. All electrolysis trials are controlled by a potentiostat (Iviumstat) using a silver reference electrode.

Electrolyte Selection

Four electrolyte systems were tested using an equimolar mixture of TiO_2/C as anode, analyzing the dissolution of Ti-ions from this anode. The base electrolytes investigated are shown in table 1. An amount of 1.25 Mol% $TiCl_2$ was added to each of these electrolytes.

Table 1: Electrolytes tested (all containing additional 1.25 Mol% $TiCl_2$)

Base electrolyte	**Melting point [°C]**	**Process Temperature [°C]**
$(KCl\text{-}LiCl)_{eut.}$	353	387
$(KBr\text{-}LiBr)_{eut.}$	329	383
$(LiBr\text{-}CsBr)_{eut.}$	289	382
$(LiJ\text{-}CsJ)_{eut.}$	217	297

All electrolytes were based on alkali halides due to the fact that these chlorides have the lowest solubility for TiO_2 and it is assumed that the same accounts for the bromide and iodide systems.

The dissolution mechanism of the anodes was analyzed in a first step by linear sweep voltametry. All sweeps were done at scan rates of 1 mV/s resp. 0.5 mV/s up to the evolution of the corresponding halide (Cl_2, Br_2, I_2). An example displaying the result of the linear sweep plot in the $KCl\text{-}LiCl\text{-}TiCl_2$ system is shown in Figure 3.

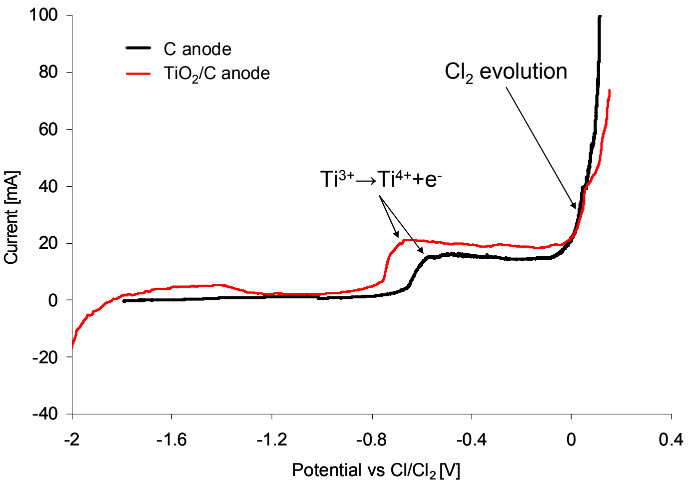

Figure 3: Linear sweep of a C and a TiO_2/C composite anode in the KCL-LiCl-$TiCl_2$ electrolyte

As can be seen only one anodic reaction is proceeding before chlorine evolution. According to literature [4] this reaction should correspond to the $Ti^{3+} \rightarrow Ti^{4+}$ oxidation. If this is true it will be not possible to dissolve titanium ions with lower valences than Ti^{4+}. To proof this, electrolysis trials were conducted at two different potentials. The first experiment was conducted at a potential slightly lower than the reaction potential (about -0.81 V) and the second one at a slightly higher potential (about -0.51 V). After each experiment the electrolyte and the off gas washing water were chemically analyzed.

Experimental Results

After exposing the composite anode to the electrolytes, the same chemical reaction (6) proceeds in all electrolytes, leading to increased amounts of titanium in the electrolyte. This reaction transfers all two valent titanium to the valence of three and relocates the reaction potential and increases the current (Figure 3).

$$TiO_2 + TiCl_2 \rightarrow 2TiOCl \tag{6}$$

All electrolytes investigated showed the same characteristics in their linear sweeps. One reaction always occurs at the same potential difference to Cl_2 and then Cl_2, Br_2 or I_2 evolution. The chemical analysis revealed that the appearing peak can be attributed to the oxidation of Ti^{3+}. Therefore it is not possible to dissolve TiO_2 with a lower valence than $^{4+}$. As a consequence, chloride and bromide based electrolytes can not be used, as the evaporation point of $TiCl_4$ is 136°C and that of $TiBr_4$ is 230 °C, both significant below the lowest possible process temperature. Consequently the solubility of Ti^{4+} in the tested chloride and bromide based electrolytes is extremely low, which was also proofed by the electrolysis trials and the high amounts of titanium in the off gas scrubbing water when using chloride and bromide based systems. The only possible electrolyte system seem to be a iodide based one, and the only possible mechanism is a iodiniation of the anode followed by a dissolution and reduction of TiI_4 according to (1) - (3). But for this process an intermediate (auxiliary) electrode will be necessary for prereduction in order to prevent unwanted reactions between Ti^{4+}-ions and the deposited metallic titanium.

ANODE MODELLING

The anode is a mixture of carbon and TiO_2 powder. To ensure the aimed semicontinuous process it is not feasible to use block anodes which would be better, as one of the requirements for a reliable electrode is its electrical conductivity. But the electrical conductivity of a powderized anode mix is lower than that of pressed anode due to its smaller contact area and is strongly dependent on the carbon content of the anode as can be seen from figure 4. Main reason for that is the low electrical conductivity of TiO_2. Figure 4 shows that the best compositions are reached at C/TiO_2 ratios above 2.

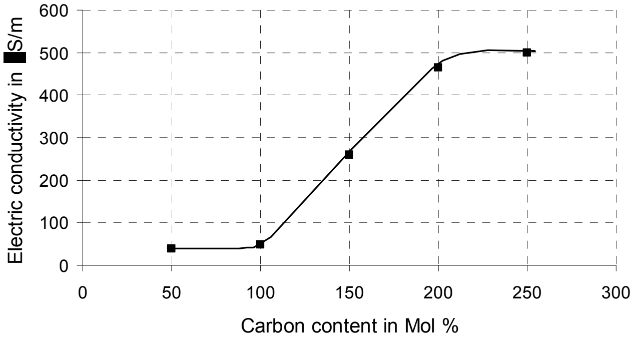

Figure 4: Electrical conductivity of a pressed TiO_2+C mixture at room temperature [3]

The optimal C/TiO_2 ratio according to the chlorination reaction, which is assumed to be similar to the iodation process, is investigated in the next step. The gross reaction of the proposed process (7) shows a simultaneous reaction between two solids and a gaseous compound at the same time.

$$TiO_2 + 2C + xCl_2 \rightarrow TiCl_x + 2CO/CO_2 \tag{7}$$

This kind of reaction is quite unlikely and therefore the reaction mechanism has been investigated more in detail by W. E. Dunn [4]. He discovered that the overall reaction is proceeding via the shrinking particle model, so the optimal composition is the stoichiometric composition. Excess carbon results in carbon layer formation, decreasing the reaction rate. Therefore the chemical composition of the anodes is fixed according to the process temperature. The stoichiometric C/TiO_2 ratios were calculated and plotted versus the temperature (Figure 5).

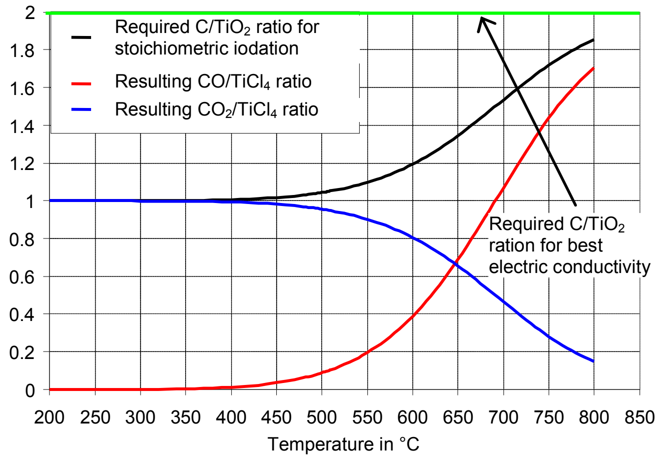

Figure 5: Stoichiometric Anode composition in correlation with the temperature

Figure 5 shows that the stoichiometric composition is strongly dependent on the temperature. The required C/TiO_2 ratio of 2 can just be achieved if only CO is formed during the process. According to the Boudouard equilibrium this is only possible at significant higher temperatures than 800 °C. The evaporation point of all Titanium-halides including TiI_4 (377 °C) is lower than 400 °C, so the maximum process temperature must be far below 800 °C most probably below 350 °C. The consequence is that the anodes in the suggested process will not have the optimal electric conductivity.

In order to improve the anode conductivity technically an increase of the contact area by variation of the particle sizes might be possible. Another way of influencing this critical parameter might be the use of different carbon sources like tar and coal. An advantage of tar for example is the improved contact between TiO_2 and C, but on the other hand, the C content of the anode is not predictable due to evaporation of volatile arenes

CONCLUSION

A modified anode concept for molten salt titanium electrolysis is suggested and investigated. This process is based on an in-situ halidation of TiO_2 in the electrochemical process. The reaction shall take place in the same reactor and simultaneous to the $TiHal_x$-reduction at temperatures below 600 °C.

First investigations, analyzing different electrolyte systems by linear sweep voltametry showed that the dissolution of Ti-ions from the anode will be as Ti^{4+}. This results in the fact that $TiCl_4$ and $TiBr_4$ are volatile even at the lowest possible process temperature for chloride/bromide systems. Therefore the only suitable electrolyte system seems to be iodide based. The second challenge is the investigation of the anode electrical conductivity and the influence of carbon content, grain size and carbon source on this property. This will be done by impedance analysis using a two electron setup. Finally a third project task is the necessity to work with an intermediate electrode to prevent reactions between Ti^{4+} and the deposited metallic titanium. The development of this intermediate anode will be done in future parallel to the verification of the proposed and explained anode process and the optimization of the anode electric conductivity.

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Molten salt electrolysis of Titanium using a TiO_2-C composite anode in halide electrolytes

- proof of concept -

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Prof. Dr.-Ing. Bernd Friedrich

Aim of the Invention

Aim:

Development of a fast, cheap and semi continuous process for titanium production at moderate temperature (≤ 600 °C)

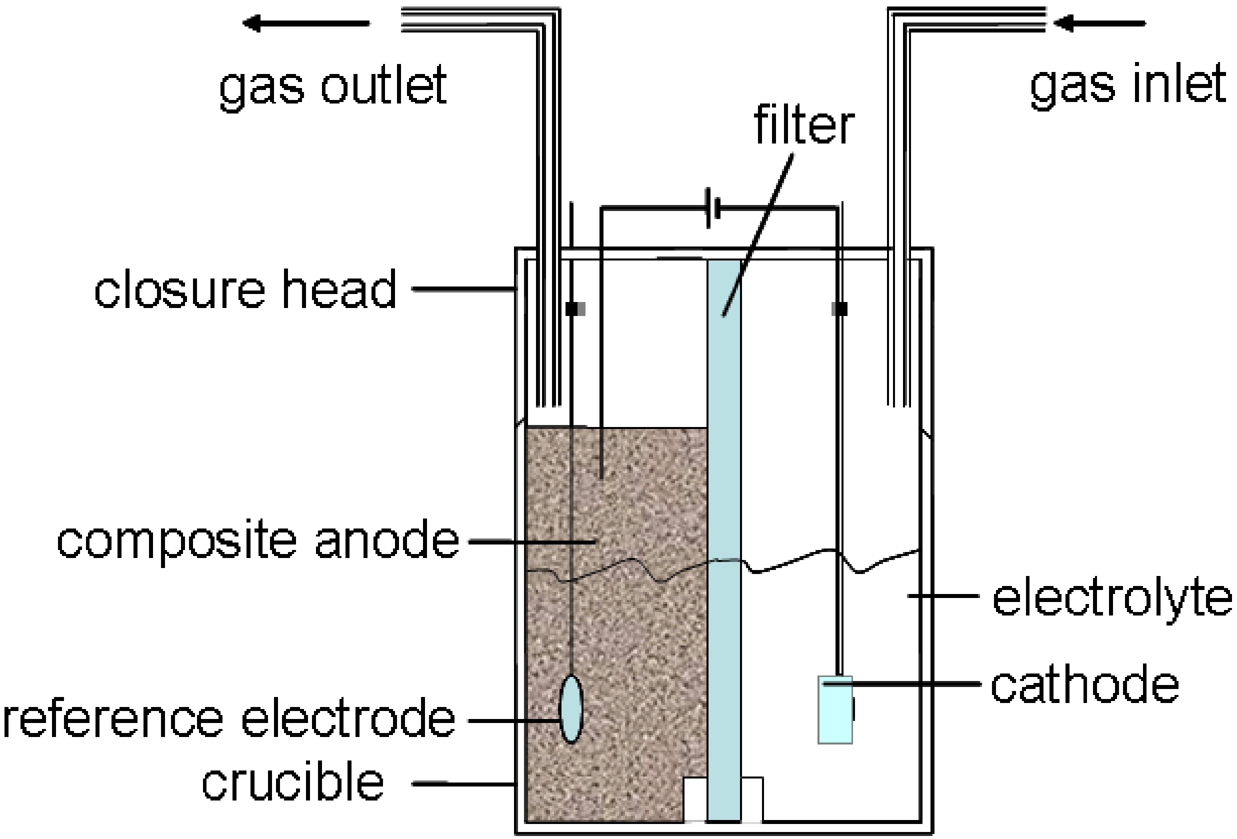
Invention:

Molten salt electrolysis process including supply of Ti-ions by in-situ halidation of a TiO_2-C composite anode

Tasks:

- Design of a suitable electrolysis setup
- Development of a composite anode
- Selection and testing of electrolytes
- Evaluation of process parameters

Principle



$TiHal_x \rightarrow Ti^{x+} + xHal^-$

anodic reaction:
$TiO_2 + 2C + xHal \rightarrow TiHal_x + 2CO/CO_2$

cathodic deposition:
$Ti^{4+} + e^- \rightarrow Ti^{3+} + e^- \rightarrow Ti^{2+} + 2e^- \rightarrow Ti$

Titanium valences within the electrolyte

Disproportion reactions within the electrolyte:

$$Ti + 3Ti^{4+} = 4Ti^{3+}$$

$$Ti + Ti^{4+} = 2Ti^{2+}$$

- metallic titanium gets re-dissolved after deposition, decreasing the current efficiency of the trials
- the composition of the electrolyte is permanently changing causing e.g. freezing of the electrolyte
- Ti^{2+} deposition is proofed and working

Optimal titanium valence within the electrolyte is +II

Composite anode

…. but the composite anode contains TiO_2

- the value of Ti within the anode is +IV
- at T ≤ 600 °C no reduction with C takes place

→ all Ti dissolving from this anode should be four valent

However:

According to a Russian literature source from the 60’s it is possible to dissolve titanium with lower valences

➡ **experimental proof is needed**

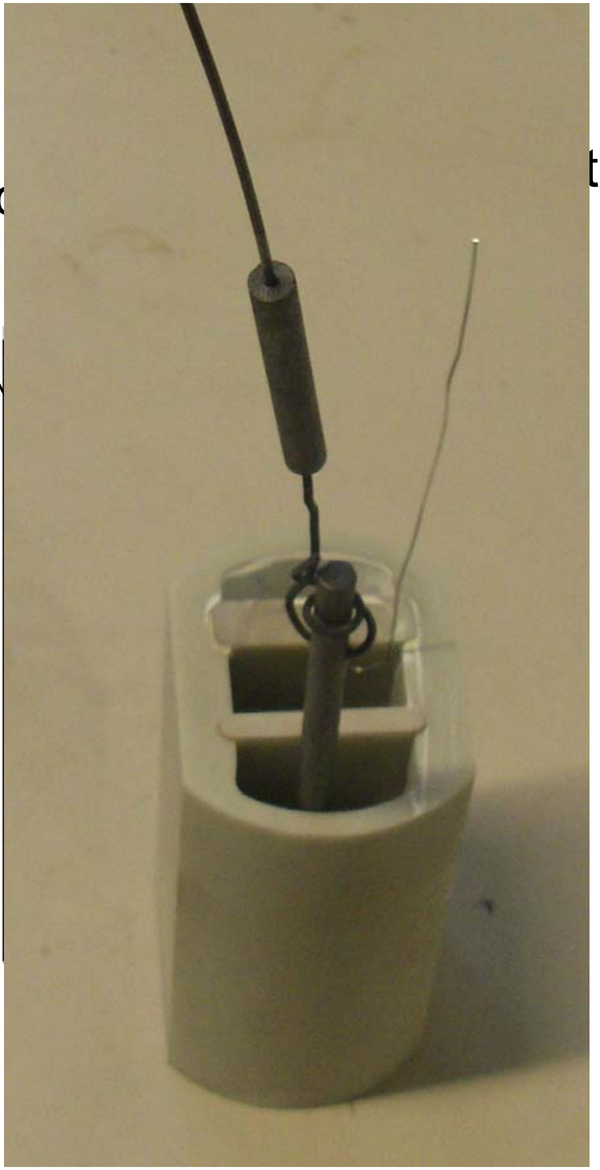
Experimental setup – Crucible selection

Requirements:

- chemical stability versus Ti^{2+}-halides
  → no oxide based materials feasible
- super low electrical conductivity
  → no metal or carbon crucibles possible

→ experiments showed chemical stability of AlN and BN

- mechanical stability during solidification of the electrolyte
  → no BN

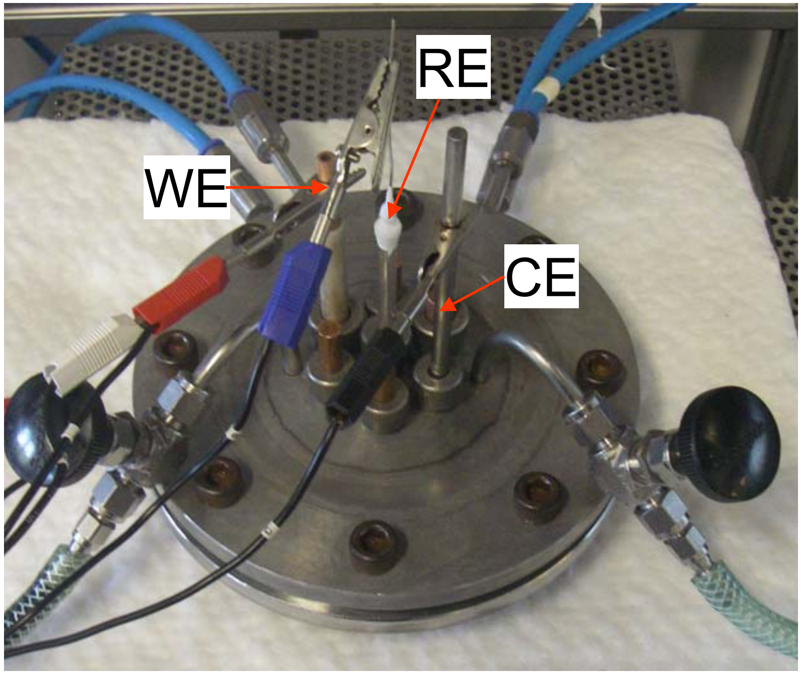


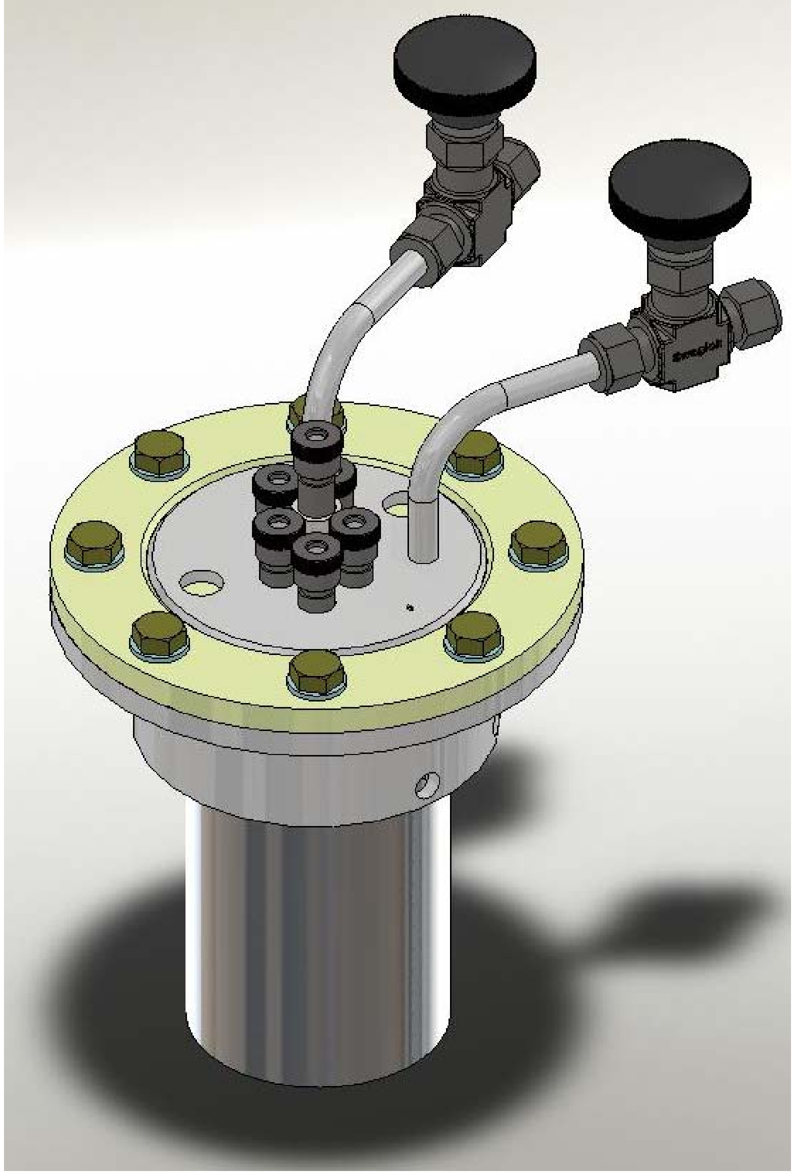
AlN cruc

ts

Experimental setup – advanced cell design

- crucible is set in a steel cell
- water cooled lid with airtight fittings
- flushed with Ar
- off gas passes a washing bottle
- control by potentiostat using a silver reference





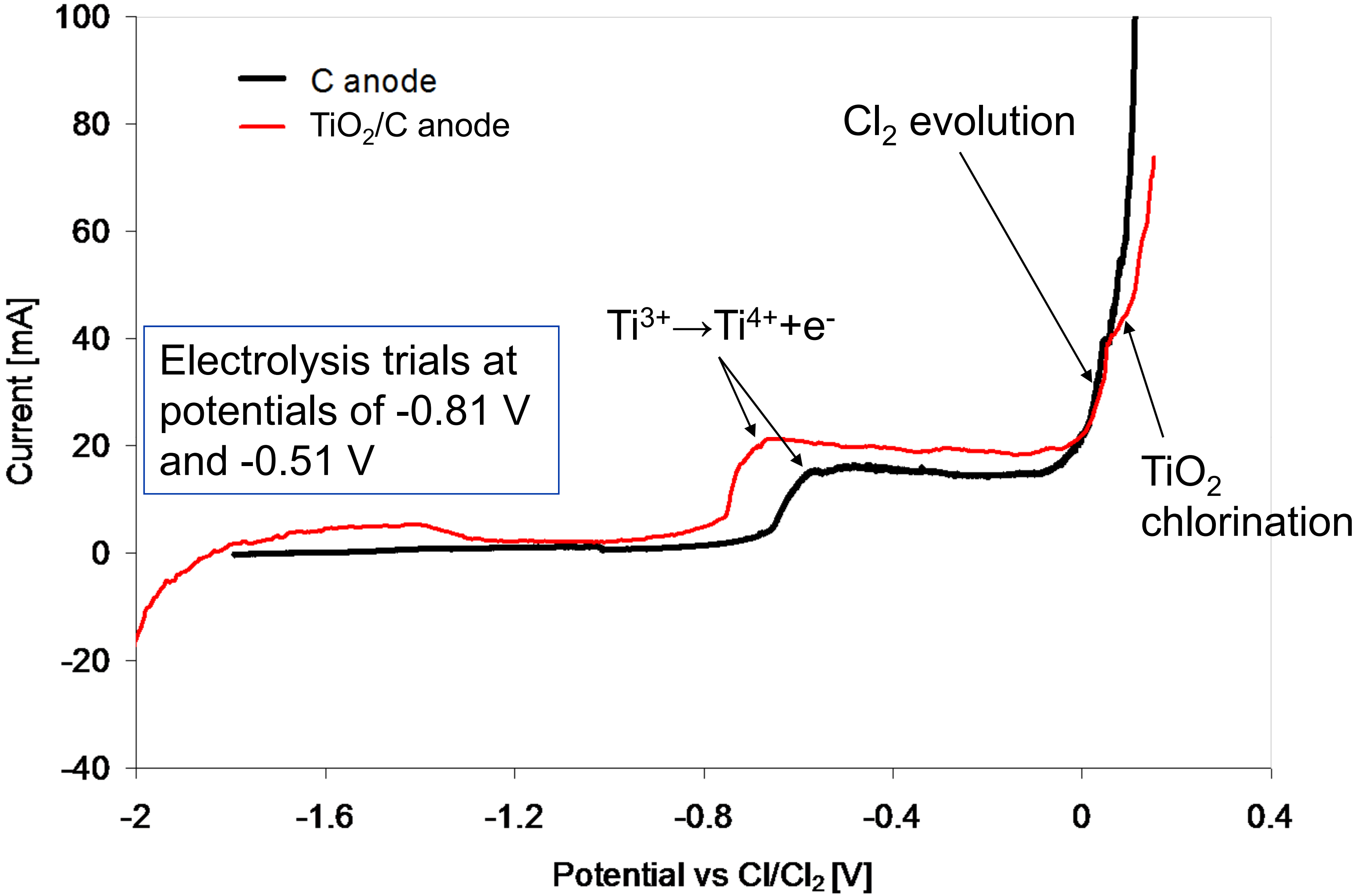
Experimental parameters

- Different base electrolytes were tested:

Base electrolyte	**Melting point [° C]**	**Process Temperature [° C]**
$(KCl\text{-}LiCl)_{eut.}$	353	387
$(KBr\text{-}LiBr)_{eut.}$	329	383
$(LiBr\text{-}CsBr)_{eut.}$	289	382
$(LiJ\text{-}CsJ)_{eut.}$	217	297

- 1,25 Mol% $TiCl_2$ was added to each electrolyte
- Anode material: Carbon and C/TiO_2 ratio = 1
- Linear sweeps up to $Cl_2/Br_2/I_2$ evolution
- Electrolysis at two adjusted potentials
- Chemical analysis

Linear sweep of the KCl-LiCl-$TiCl_2$ system



Electrolysis trials at potentials of -0.81 V and -0.51 V

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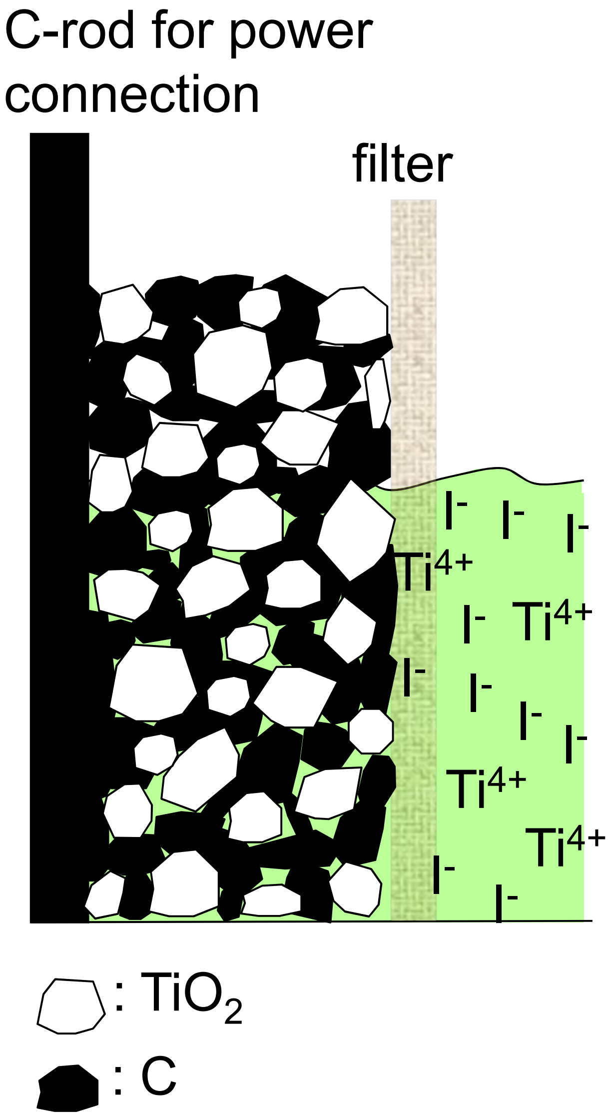
Experimental results

- all electrolytes show the titanium related reactions
- it is not possible to dissolve titanium with a lower valence than +IV

Consequence:

- an intermediate electrode is always required to get Ti^{2+}
- chloride and bromide based electrolytes can not be used (Evaporation of $TiCl_4$ = 136 °C, $TiBr_4$ = 230 °C)
- iodide based electrolytes are promising due to the higher evaporation point of TiI_4 (377 °C) corresponding to the base electrolyte (e. g. $(LiJ\text{-}CsJ)_{eut.}$)

Anode Concept



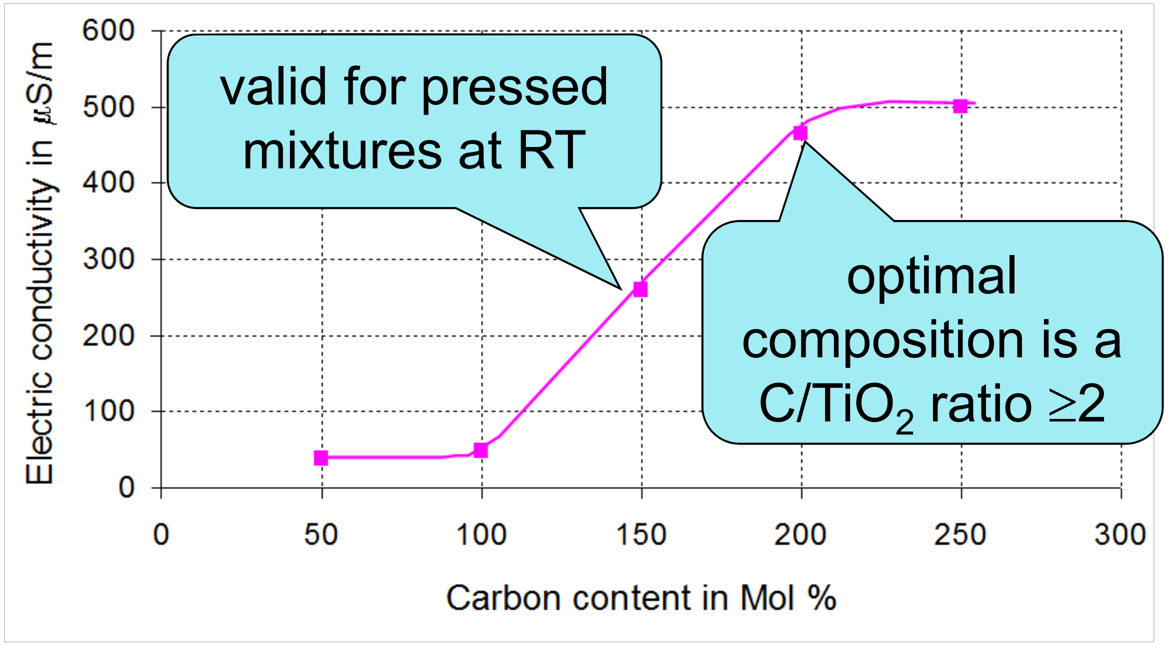
source: Gusin, 1963

gross reaction:

$$TiO_2 + 2C + 4I \rightarrow TiI_4 + 2CO/CO_2$$

requirements:

- porosity for fast kinetics
- good electrical conductivity



valid for pressed mixtures at RT

optimal composition is a C/TiO_2 ratio ≥2

Halidation Mechanism for packed beds

- iodation is assumed to proceed similar to the chlorination mechanism

- overall reactions:

$$\left.\begin{aligned} TiO_{2(s)} + 2I_{2(g)} + C_{(s)} &\rightarrow TiI_{4(g)} + CO_{2(g)} \\ TiO_{2(s)} + 2I_{2(g)} + 2C_{(s)} &\rightarrow TiI_{4(g)} + 2CO_{(g)} \end{aligned}\right\}$$

simultaneous reaction, dependent on temperature

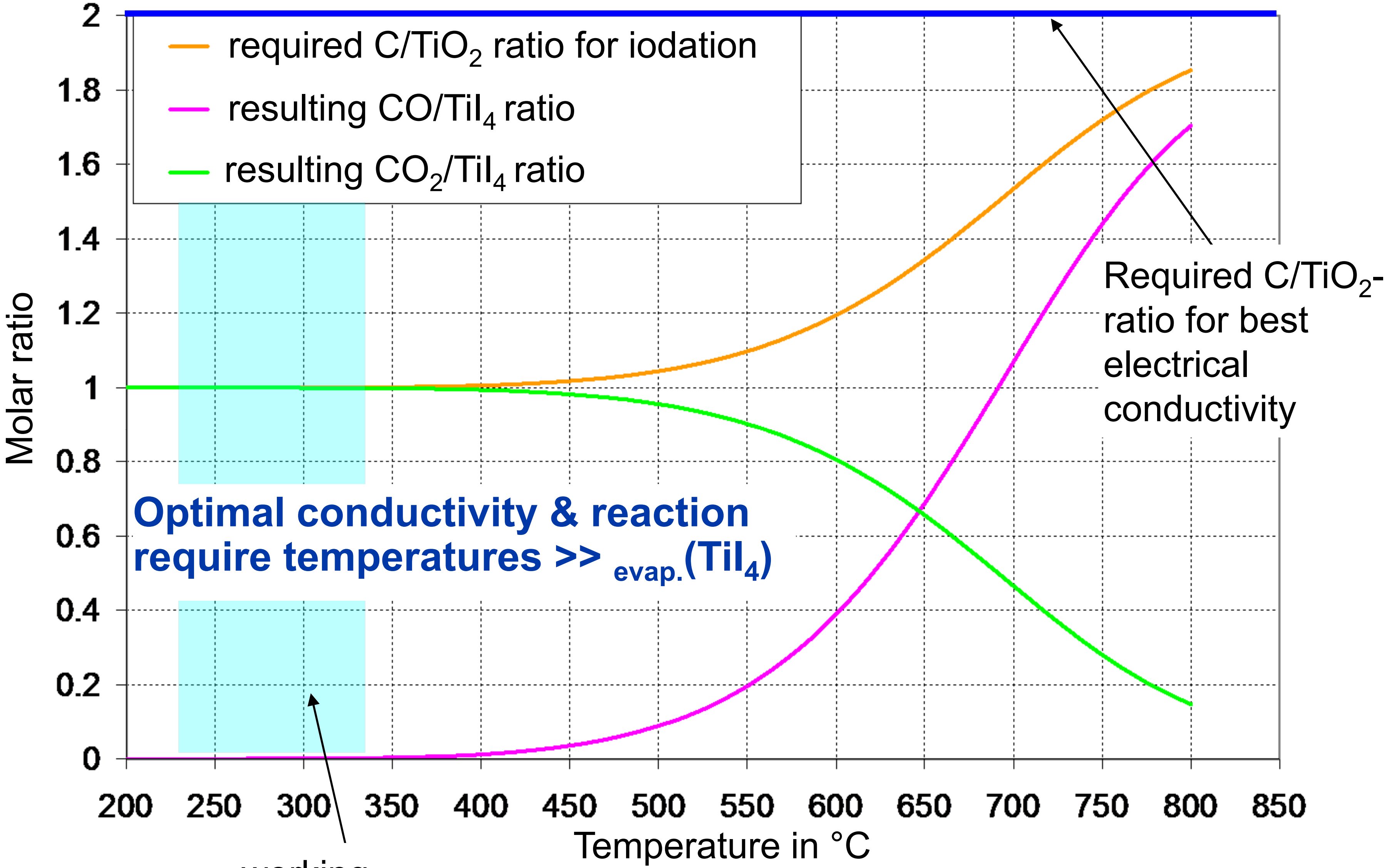
- reaction model*: shrinking particle

→ optimal is the stoichiometric composition!

→ excess carbon results in carbon layer formation decreasing the reaction rate

*Source: Dunn, 1979

Calculation of Anode Carbon Content



Optimal conductivity & reaction require temperatures >> $_{evap.}(TiI_4)$

Required C/TiO_2-ratio for best electrical conductivity

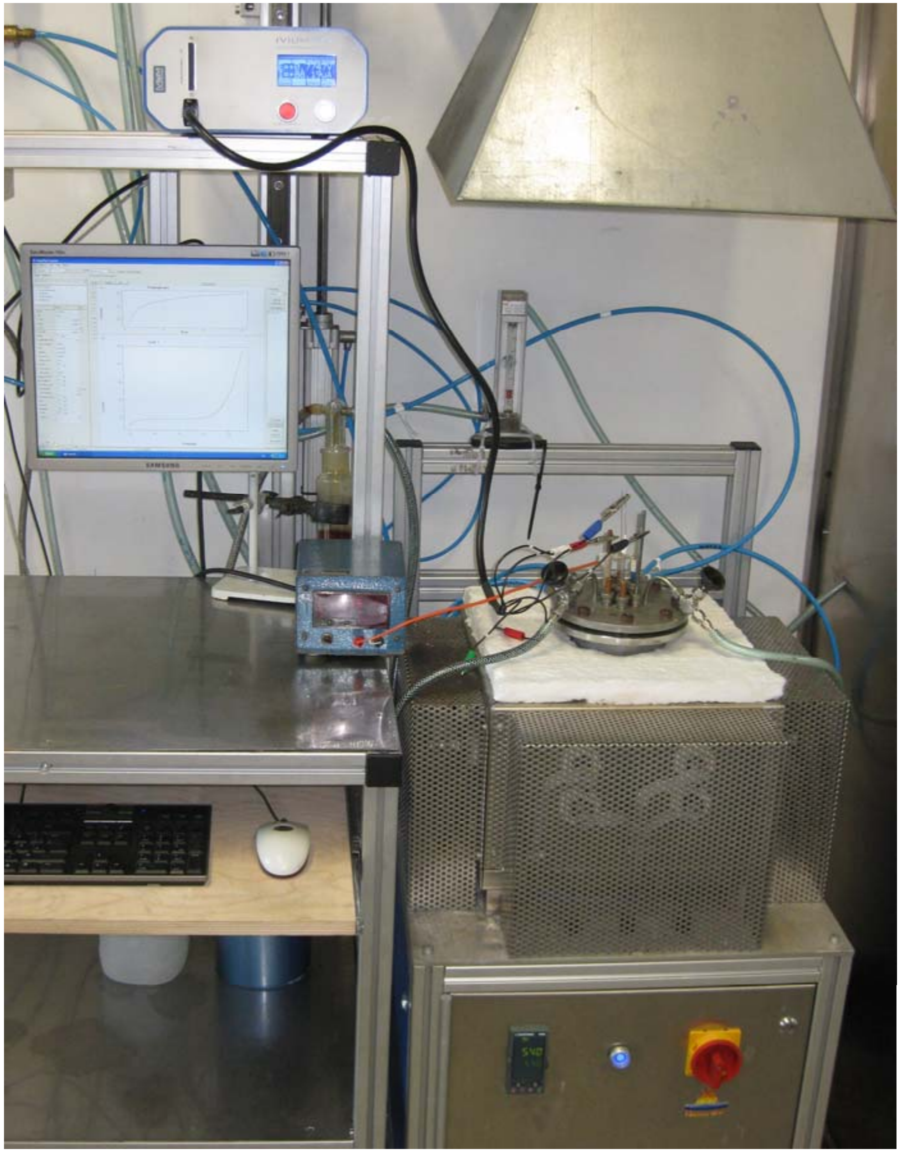
working temperature

Summary

- AlN electrolysis cell was designed and is suitable
- it is not possible to dissolve Ti with lower valences than +IV from a TiO_2/C anode
- only TiI_4 can be kept within the electrolyte
- in-situ iodination seems to be a possible process for supplying Ti-ions to the electrolysis.
- chemical composition of the anodes is fixed according to the aimed process temperature (for stoichiometric reaction)

Future Work

- development of an intermediate electrode
- long time test of the proposed process
- optimization of the anode electrical conductivity
- investigation of further iodide based electrolytes
- determination of process parameters (e. g. current density)
- successful Ti deposition



Thank you for your attention

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