CONSIDERATIONS FOR AN INNOVATIVE HIGH TEMPERATURE BATTERY IN POWER PLANT APPLICATIONS

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Abstract:

A novel high temperature battery based on the concept of the solid oxide fuel cell (SOFC) is presented. Due to the use of cheap iron- and calcium-based storage materials providing a high theoretical capacity of roughly 1300 Wh/kg the battery could be used to optimize the part load properties and the long term durability of conventional power plants. The elevated working temperature of 800 °C makes it applicable where high quality heat is available and needed. In this paper an economical consideration leads to general design recommendations for this battery which operates in test mode with current densities of 150 mA/cm^2 and approximately one hour charging/discharging time at cell voltages between 0.7-1.2 V.

1   Introduction

Any technology for storing electrical energy provides the opportunity of decoupling generation and usage of electricity. This can be beneficial whenever there is a temporal change of electricity generation cost due to load variation or fluctuating availability. Latter becomes especially true, when augmenting the grid with power sources (renewables) with a possibly large discrepancy between actual and rated power input. In this case, energy storage can substitute the increase of rated power or even render additional flexible power plants unnecessary.

Since conventional storage technologies (e.g. pumped hydro) lack the possibility of expansion, electrochemical storage can be an alternative. However, due to high investment cost this option has not been implemented on significant scale so far. Therefore technological alternatives with low investment cost are needed. A very innovative concept that fulfills these requirements is the Rechargeable Oxide Battery (ROB) which will be presented in this paper.

1.1 Technology

The Rechargeable Oxide Battery (ROB; Fig. 1) is based on a reversible solid oxide cell (SOC, Jülich F10-design, [1, 2]) that operates in turns as fuel cell and as electrolyzer. The SOC is coupled with a storage material which provides and absorbs reactants at the fuel side. Whereas a classical fuel cell or electrolyzer system needs continuous delivery and removal of fuel gases the integrated storage material enables the system to be operated as a battery in a semi-closed system. At the fuel side no pumping is needed. At the air side a simple passive air vent or a small fan suffices. This saves all cost related to gas delivery and conditioning.
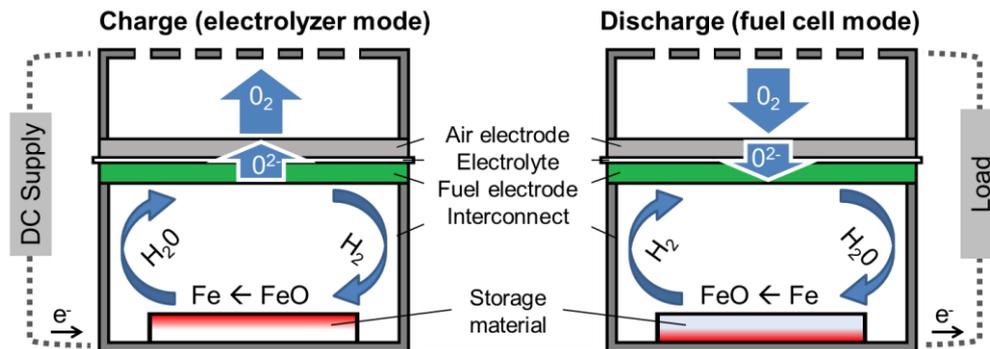
Fig. 1: Schematic of working principle of ROB in charge and discharge operation according to [3]

As depicted in Fig. 1 in discharge operation a metal is oxidized by steam yielding hydrogen. In the same manner as in a fuel cell hydrogen is the oxidized by oxygen-ions that diffuse from the air side through the electrolyte forming again steam. The electrons that are set free in this reaction can be used to supply a load with electricity. The battery is discharged when all of the metal base storage material is oxidized. Vice versa, in charging operation the metal oxide is reduced, leading to steam which is electrolyzed into hydrogen which acts as reducing agent for the metal oxide.

Below, the governing chemical equations of the ROB system are shown, where *Eq. 1* describes the reversible reaction of the atmosphere with the storage material and *Eq. 2* and *Eq. 3* represent the well-known reactions at the respective electrodes of the SOC.

$$3Fe + 4H_2O \leftrightharpoons Fe_3O_4 + 4H_2 \qquad\qquad Eq. 1$$

$$H_2 + O^{2-} \leftrightharpoons H_2O + 2e^- \qquad\qquad Eq. 2$$

$$O_2 + 4e^- \leftrightharpoons 2O^{2-} \qquad\qquad Eq. 3$$
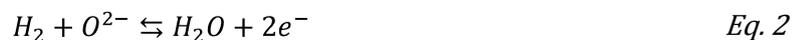
1.1.1 Operating Conditions

Due to the use of yttria stabilized zirconia (YSZ) as electrolyte elevated temperatures of 600 °C-800 °C are necessary to provide a sufficiently high ionic conductivity of the electrolyte. Also, the redox reaction of the storage material favors this temperature range. Usually, in solid oxide fuel cells (SOFCs) hydrogen is humidified up to 20 % steam content to not reduce the YSZ-based electrolyte. In solid oxide electrolysis cells (SOECs), during electrolysis of steam, about 20 % hydrogen is added in order to safely avoid oxidation of the

nickel containing fuel electrode. Hence the operating conditions for the ROB are at 800° C and steam-to-hydrogen rations between 1:4 and 4:1 respectively.

1.1.2 Application

Using iron-based storage material, the battery provides a cheap way of storing energy at a capacity of roughly 1,300 Wh/kg. First experiments show that the battery in the current design displays charging/discharging durations of about one hour and current densities of 150 mA/cm^2 at a cell voltage of approximately 0.7-1.2 V.

Possibly, the main advantage over other electrochemical storage devices such as lithium-ion batteries is the lower investment cost of used materials. Compared to conventional SOEC/SOFC systems, especially the operating cost will be lower mainly due to avoided gas conditioning (purity, storage, pumping, metering and thermal losses).

From the specific technical operation conditions of the battery – especially the temperature – two applications are most promising: Firstly the operation of the battery in high frequency for stabilization purpose of the electricity network. Provided a good insulation is applied the frequent charging and discharging of the battery keeps it at operating temperature. Secondly, the operation in combination with conventional power plants such as gas turbines could increase the overall efficiency and durability of the system because there would be no part load operating mode.

2 Economic Considerations

The transformation of the German energy system has been characterized in recent years by the extension of fluctuating renewable electricity generation capacity such as wind (1.5 GW, 1996 – 28 GW, 2011, [4]) and photovoltaics (3 GW, 2007 - 34 GW, 2013, [5]). This development, which is currently referred to as "Energiewende", is expected to continue in the coming decades (planned for 2032: 90 GW wind, 65 GW PV, [5]). It implies the transition from a demand-oriented to a supply-oriented power generation and a spatial separation of production and consumption.

These structural changes require greater efforts to stabilize the operation of transmission and distribution networks. This includes the assurance of power quality, a stable grid frequency by power balancing and the ability to restart a collapsed subsystem without an external power supply network (blackstart). Thus, the demand for balancing power is expected to increase from 11.1 GW (2020) to 17.3 GW (2050) [6]. At the same time the changes create opportunities to boost system efficiency by peak shaving, demand-side management, renewable-induced long-term storing and associated arbitrage trading.

As technical option for the provision of network services and for the increase of system efficiency in addition to the promotion of system flexibility - by demand side management and an increase of power plant flexibility - electrical storage comes into consideration. The latter has been operated for decades in Germany as pumped storage, with an installed capacity of 45 GWh in 2013 and a power of 6.4 GW.

With the expected increase in renewable generation capacity, also the demand for storage capacity is expected to rise. Since additional construction potential of pumped storage is limited, other technologies such as compressed air, hydrogen or electrochemical storage

(batteries) could profitably enter the market and cover additional demand. However, competition to demand-side management and more flexible power plants has to be considered.

The economic potential of currently available battery systems to increase system efficiency during the transformation of the energy system is low. Scenarios with limited fossil energy production due to climate protection goals show that the storage of electrical energy is inevitable as the renewable energy share exceeds 80% of total electricity production [7]. However, almost exclusively hydrogen and methane (Power-to-gas) storage technologies are used for the long term storage requirements. Nevertheless, novel battery concepts with a more favorable cost structure than lithium-ion technology could enter the market. Their potential has to be large enough to offset the development advantage and to compete with established technologies under short-term consideration. Also, the regulatory framework would have to be adjusted.

In addition to the efficiency-enhancing applications described above the regulatory framework and recent reductions of the feed-in rewards for electricity from PV systems provide an increased feasibility for decentral battery storage. Also, using battery systems in combination with a carbon fuel based engine (diesel generator, gas turbine, etc.) allow the operation of the engine in the optimum efficiency range which increases lifetime and reduces fuel consumption and emissions.

One focus of current research projects is the development of batteries for the mobile as well as stationary use. This also reflects in a number of recent demonstration projects, where stationary battery storage is tested for the provision of network services, in smart grid systems and in combination with photovoltaic systems.

Against the background of an emerging and open market for storage systems, commercial lithium ion batteries are not always a profitably applicable technology due to high investment costs that are related with the use of expensive materials. For example, in a lithium ion battery (NCM-type), the share of material costs in the overall investment cost reaches more than 50% and is mainly caused by the cathode elements nickel, cobalt and manganese [8].

Regardless of whether the unexpectedly sharp fall in the price of these systems continues the ROB approach provides a significant potential to reduce cost through the use of ferrous material and it is also advantageous from the viewpoint of environmental protection and sustainability. The latter is due to the use of non-toxic iron for which a comprehensive recycling infrastructure exists.

Lower material cost of the ROB are, however, accompanied by higher operating costs to maintain the operating temperature of 800°C and a lower efficiency than lithium ion. Whether this results in a net cost advantage for the ROB, is dependent on the specific application, the number of charge cycles and the design parameters (voltage, current desities, use of heat). Conclusions can only be drawn after completion of the measurement series and further extensive research.

3   Experimental

Experimental work is conducted with the aim to optimize material properties of the storage material, specifically to increase capacity and kinetics while at the same time to reduce

degradation effects and establish a lower operating temperature. In order to reduce cost, different manufacturing routes of the storage material such as tape-casting and extrusion are being investigated.

3.1   Material development

As was mentioned before, battery performance and cost depend on the degradation properties of the actual storage material. When pure iron as storage is used two general challenges emerge: particle agglomeration and layer formation. This can be seen in Fig. 2. The iron oxide (Fe_2O_3) in as-sintered state (900 °C in air for 3h, 5K/min heating rate) is initially fine-grained. During first reduction (charging, 800°C, 10h in Ar-4%H_2) the metallic iron sinters further forming iron agglomerates

a)   As sintered

b)   First reduction (1 halfcycle)

c)   Oxidized after 10 halfcycles

d)   Reduced after 11 halfcycles
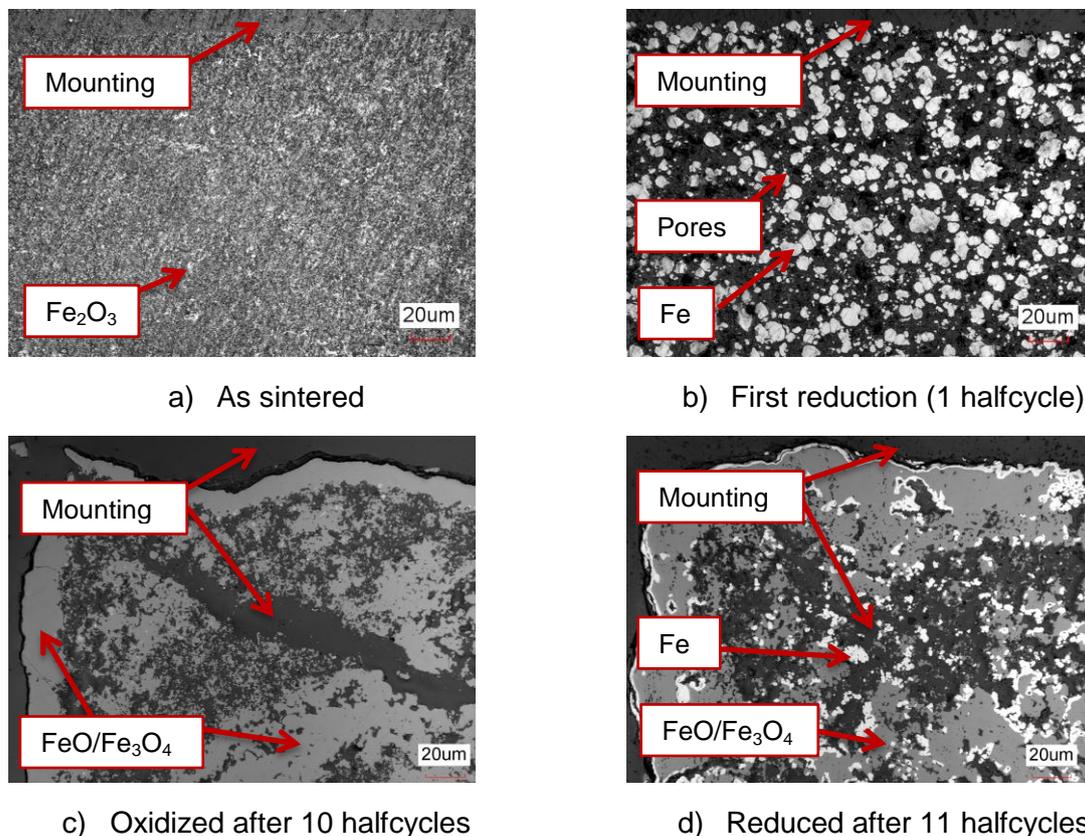
Fig. 2: Cross-sections of pure iron storage material after sintering (a), first charging (b) and after 10 (c) and 11 (d) halfcycles respectively [3]

During oxidation under above mentioned conditions (discharging, 800 °C, 10h, steam-to-H_2-ratio 4:1) iron forms layers of oxide products at the surface (here FeO and Fe_3O_4). The growth of these layers is quick at first until the process is controlled by the outward diffusion of iron species [9, 10, 11]. This means that the diffusion rate of iron through the product layer is faster than the inward diffusion of gaseous species. As a consequence, an area of apparent iron depletion occurs slightly below the surface.

Conversely, during reduction (steam-to-H_2-ratio 1:4) a layer of metallic iron forms at the surfaces. Due to sintering these layers quickly inhibit further gas transport to the Fe/FeO interface and reduction of iron oxide slows down significantly.

To cope with both effects, further oxides were added to the iron oxide based active material. As an inert oxide support 30 vol.% YSZ was added in order to separate single iron oxide particles from each other and thus keep them from sintering. The effect on the microstructure can be seen in Fig. 3.

a) As sintered

b) First reduction (1 halfcycle)

c) Oxidized after 10 halfcycles

d) Reduced after 11 halfcycles
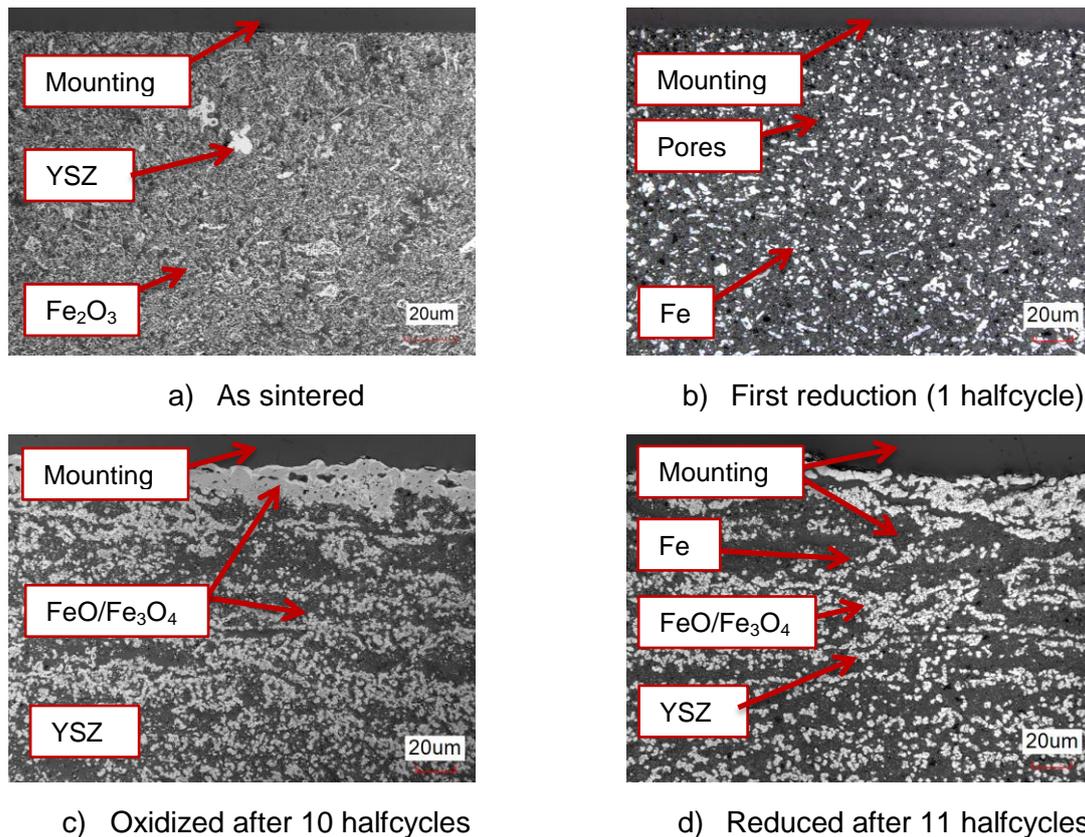
Fig. 3: Cross-sections of iron storage material with 30 vol.% YSZ as inert oxide matrix after sintering (a), first charging (b) and after 10 (c) and 11 (d) halfcycles respectively

The addition of YSZ leads to a significant reduction of particle agglomeration as well as layer formation. Moreover, the built layers show a higher porosity leading to a better gas transport into the inner regions of the storage material. However, layer formation still takes place after an increased number of charging-discharging cycles (20 full cycles) and layers of greater thickness and density occurred.

In search of a suitable second oxide several oxides were benchmarked as described elsewhere [3]. As a result CaO was identified to be most promising. After 10 full cycles no permanent layer formation occurred and also particle agglomeration was reduced (Fig. 4). The good degradation properties are possibly due to the reversible formation of mixed oxides of CaO and Fe_2O_3 namely $CaFe_2O_5$, $CaFe_5O_7$, $CaFe_3O_5$ and the thereby changed properties of iron diffusion and sintering. These phases, earlier investigated by several authors [12, 13, 14, 15] were detected in XRD measurements of the system described in [16]

a) Discharged state (10 halfcycle)   b) Charged state (11 halfcycle)
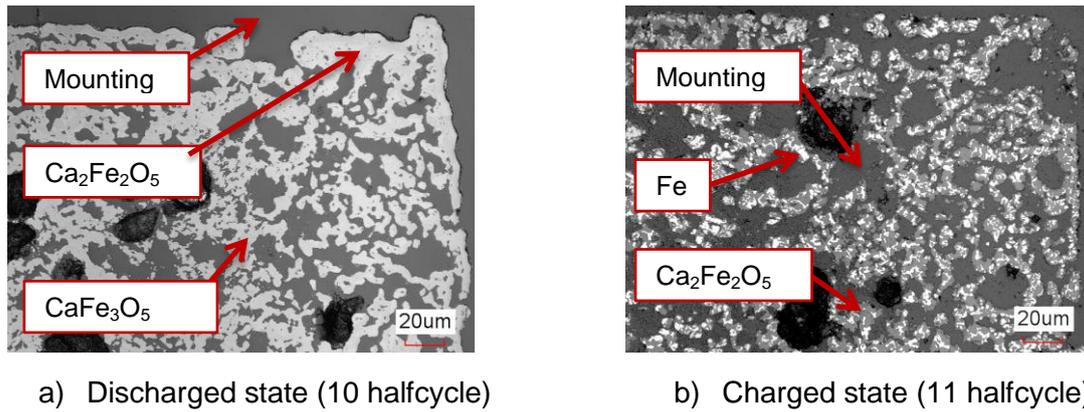
Fig. 4: Calcium iron oxide after sintering at 900 °C and subsequent redox treatment a) discharged (oxidized) state and b) charged(reduced) state

Having experimentally determined a well working material combination another issue becomes the manufacturing process and its influence on material properties.

3.2 Manufacturing route

For material screening purposes most of the time a laboratory hand press was used to produce samples. However, for a larger amount of sample material and for repeatable and reproducible results storage components have to be manufactured with an easier and more convenient route. This can be done by means of tape casting or extrusion. Fig. 5 depicts the general working principle of both techniques and exemplary sample geometries are shown.
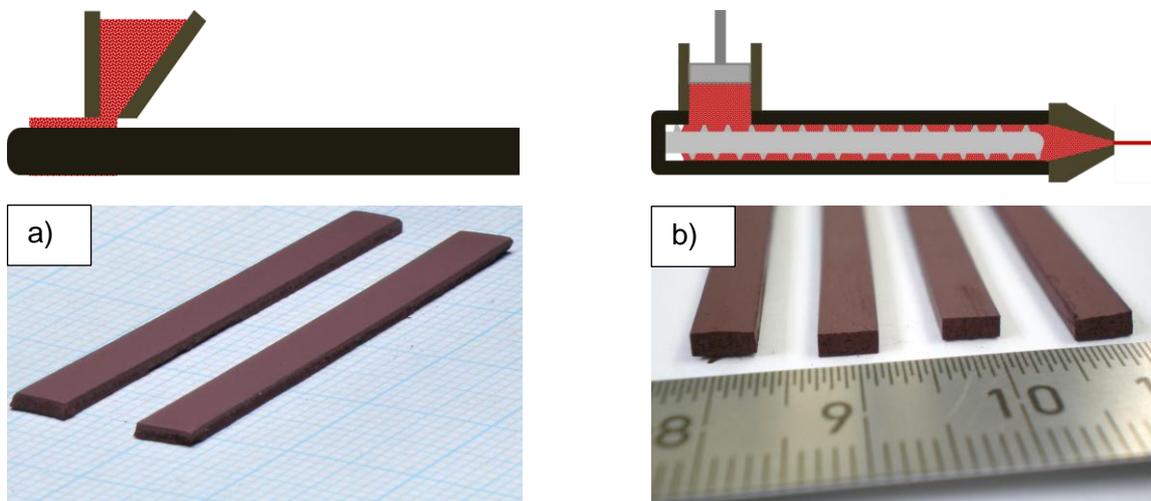
Fig. 5: General schematic of the considered possible manufacturing routes tape casting and extrusion and exemplary samples made by a) tape casting and b) extrusion. Extruded samples can have a large variety of cross sections whereas tape cast-samples are limited to approximately 1 mm thickness.

3.2.1 Tape casting

Tape casting is a process, during which a slurry is evenly distributed on carrier tape. Via a doctor blade the height of the resulting (dried) tape can be adjusted within a range of 1 mm down to a few µm.

Tape casting could be readily used due to the availability of a well-working slurry recipe reported in [17]. Slurries were produced without cracks when $CaCO_3$ instead of the above mentioned CaO was used. This has the advantage of generating additional porosity upon

sintering and also problems related to the strong hygroscopy of CaO can be overcome. After casting, samples and actual storage parts were die-cut out of the generated tape, sintered and then used in the battery prototype (see section 4).

3.2.2 Extrusion

During extrusion a Fe_2O_3 and $CaCO_3$ based paste is near-net shaped by pressing the paste trough a round or rectangular die. Like this storage components with a thickness greater than 1 mm can be directly manufactured. Also, the applied paste uses water as solvent, which makes it economically and environmentally more feasible than the organic slurry in the tape casting process. However, the development of the extrusion paste is non-trivial which is why there is still research to be done to manufacture larger amounts of storage material without cracks and without the tendency to bend during drying and sintering.

4 Battery tests

Battery tests were conducted in Jülich. An F-10 design two-cell stack was equipped with approximately 20 g of storage components per cell. The cells consist of a warm-pressed YSZ-NiO substrate, a vacuum slip-cast YSZ-NiO anode and an YSZ electrolyte. The additional diffusion barrier (ceria doped gadolinia, CGO) and the cathode ($La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, LSCF) were screen-printed on top. The tape-cast storage components were put into the gas channels of the flow field of the ferritic steel interconnect at the fuel side. Then the stack was assembled and operated at 800 °C with closed in- and outlets for the fuel. During repeated charging and discharging tests at 150 mA/cm^2 the duration of one half-cycle was found to be approximately 47 min (Fig. 6).
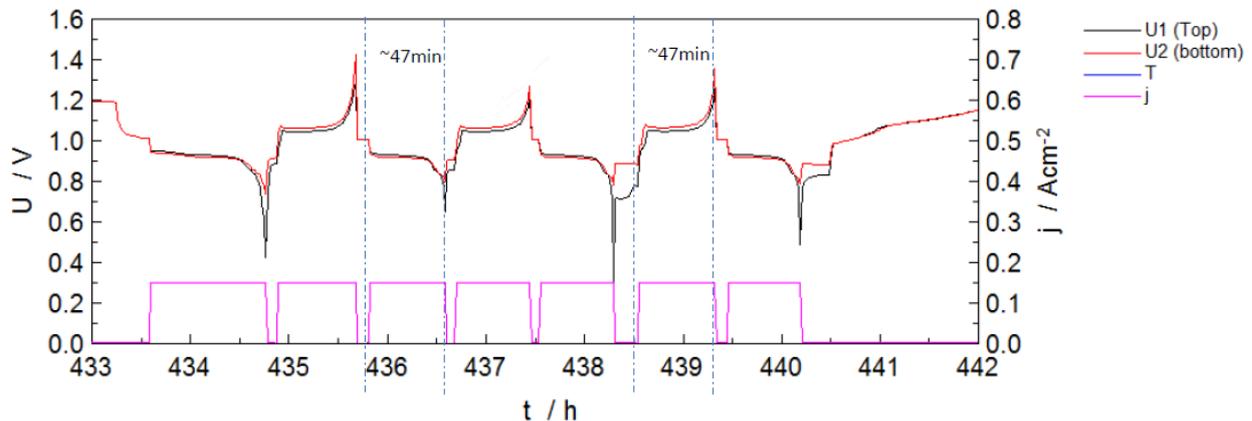
Fig. 6: Time dependent cell voltage of a two-cell stack test employing calcia-containing iron oxide based storage components during repeated galvanostatic discharging and charging with current densities of j=150 mA/cm^2 at 800 °C.

To further increase the capacity and the current density the total mass of the employed storage material per cell area needs to be increased while at the same time maintaining a high open porosity and thus an active surface area.

5 Conclusion

The experimental results of the development of a Rechargeable Oxide Battery (ROB) on the basis of a reversible Solid Oxide Cell (SOC) identify calcium oxide as most promising

candidate to be used to avoid degradation of the iron oxide based material. Tape-cast storage components on the basis of Fe_2O_3 and $CaCO_3$ were included in an two-cell stack test and galvanostatically operated for more than 200 full cycles at 800°C with current densities of 150 mA/cm^2 and a duration of 47 min per halfcycle.

Further research will focus on establishing the extrusion process for manufacturing high yield near net shape low cost storage components with a large variety of possible geometries. To establish a battery for the use in grid energy storage the general applicability of the concept needs to be further investigated. Here especially the issues of scale-up and redesign need to be dealt with.

6   Acknowledgements

7   Bibliography

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