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Electrochemical characterization of Fe-air rechargeable oxide battery in planar solid oxide cell stacks

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HIGHLIGHTS

- A novel method for testing Iron-Air oxide battery in planar SOFC/SOEC stacks.
- Electrochemical characterization of three different storage materials.
- Microstructure of the storage components after ~260 charge/discharge cycles.

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ABSTRACT

Iron-air rechargeable oxide batteries (ROB) comprising solid oxide cells (SOC) as energy converters and Fe/metal-oxide redox couples were characterized using planar SOC stacks. The charge and discharge of the battery correspond to the operations in the electrolysis and fuel cell modes, respectively, but with a stagnant atmosphere consisting of hydrogen and steam. A novel method was employed to establish the stagnant atmosphere for battery testing during normal SOC operation without complicated modification to the test bench and stack/battery concept. Manipulation of the gas compositions during battery operation was not necessary, but the influence of the leakage current from the testing system had to be considered. Batteries incorporating Fe_2O_3/8YSZ, Fe_2O_3/CaO and Fe_2O_3/ZrO_2 storage materials were characterized at 800 °C. A maximum charge capacity of 30.4 Ah per layer (with an 80 cm^2 active cell area) with ~0.5 mol Fe was reached with a current of 12 A. The charge capacity lost 11% after ~130 ROB cycles due to the increased agglomeration of active materials and formation of a dense oxide layer on the surface. The round trip efficiencies of the tested batteries were ≤84% due to the large internal resistance. With state-of-the-art cells, the round trip efficiency can be further improved.

1. Introduction

In order to reduce carbon emissions and boost energy security, increasing amounts of renewable capacity is being built up globally. Due to the intermittent nature of renewable resources such as wind and solar irradiance, the rapid growth of renewable capacity also places high demand on the electricity grid with respect to the storage of surplus electrical energy, which must be returned to the grid when electricity production falls below consumption rates when there are not enough renewable energy resources available.

Of various potential energy storage methods, a novel electrochemical energy conversion and storage system based on a reversibly operated SOFC/SOEC was first patented by Westinghouse [1] and further investigated by Siemens and different research groups [2–10]. Such an electrochemical system, a high temperature rechargeable oxide battery (ROB), comprises high temperature solid oxide cells (SOC) as energy converters coupled to a metal/metal-oxide redox as storage material. The storage material is located inside the fuel gas chamber, and does not need to make contact to the electrode. Therefore, there is no direct interaction between the storage materials and solid oxide cells. For this reason, such a battery system can also tolerate the relatively large volume change of storage materials during redox cycles, which may

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Abbreviations: ASC, anode supported cell; GDC, $Ce_{0.8}Gd_{0.2}O_{1.9}$; LSCF, $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$; MFC, mass flow controller; OCV, open circuit voltage; ROB, rechargeable oxide battery; SOC, solid oxide cell; SOEC, solid oxide electrolysis cell; SOFC, solid oxide fuel cell; WPS, wet powder spraying; YSZ, yttria-stabilized zirconia.

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otherwise damage the cells. The different reactions, i.e., redox of the metal/metal-oxide couple and electrochemical reactions at the electrode, take place in the storage material and electrode, respectively. The only thing in common, which brings these together, is the same gas atmosphere of H_2/H_2O. During charging, the battery works as an electrolyzer, using the surplus energy to produce hydrogen, which reduces the metal-oxide to metal. The water released during the reduction of metal-oxide is then consumed for further electrolysis. During discharging, the battery works as a fuel cell. The water produced (from the fuel cell reaction) at the anode oxidizes the metal into metal-oxide, releasing hydrogen for further fuel cell operation. Since only one electrochemical system is necessary for energy storage and release, and there is no need for a feed gas on the fuel side, the ROB has distinct advantages in terms of system simplicity and efficiency.

The oxygen partial pressure range, in which the redox reactions of the storage materials can take place, is limited by the cell components on one side, and the possible compositions of H_2/H_2O mixture on the other. For conventional SOCs containing zirconia-based electrolytes and nickel-based electrodes, the highest and lowest oxygen partial pressures are given by nickel oxidation and zirconia decomposition, respectively. These are 10^{-14}–10^{-43} atm at 800 °C, which correspond to the Nernst voltages of 0.71–2.25 V against air. To avoid the reduction of zirconia, the oxygen partial pressure should also be above ~10^{-36} atm (1.9 V) at 800 °C. Furthermore, for SOC stacks with metallic interconnects, Cr_2O_3 forms on the surface of the interconnect and prevent it from fast oxidation. To maintain the protective function of Cr_2O_3, the oxygen partial pressure should be above ~10^{-28} atm (1.45 V). Under these restrictions, the possible pure candidates are: cobalt, tungsten, molybdenum, iron, tin and cadmium. Sn is in a liquid state at the operating temperature, while Cd and Co are relatively toxic, and Mo and W display high vapor pressure at these temperatures and atmospheric conditions [9]. Thus iron was considered the best material choice with respect to toxicity, physical and chemical parameters, availability and costs.

The redox of the metal/metal-oxide couple and the electrochemical reaction at the fuel electrode must take place simultaneously to keep the ROB work, as the produced gas (i.e., either H_2 or H_2O) of one reaction is the reactant of the other. The 'transport' of the reactants/products between the storage and electrode can be understood by gas diffusion through the H_2/H_2O mixture in between. In this case, a stagnant H_2/H_2O mixture is an essential requirement for keeping such 'transport' occurring between the storage and electrode only. Otherwise, the ROB will not work at all. The demand on the gas tightness of the test bench, particularly on the fuel side, is therefore much higher in the case of ROB operation, since the effect of even a tiny leakage in the testing system will be predominant when there is no continuous gas flux. Ways of establishing the stagnant atmosphere in other research groups have not been well described yet. In this work, a novel method was implemented in the test bench to retain the stagnant atmosphere during ROB tests. With this method, the test bench can be easily switched between SOC and ROB modes during the test without a complicated sealing concept and gas manipulation process. Such a concept can also be employed in energy systems, in which fuel cells are desired to operate between SOC and battery modes. The electrochemical properties of the storage material and ROBs can be characterized with conventional test bench and stacks after only small modifications. This is especially important in terms of time and cost when the storage materials remain in the R&D phase.

Previous studies [9,10] have shown that pure iron does not work optimally as a storage medium, because the microstructure is too dense and a dense layer also forms on the surface after several redox cycles, both of which prevent the ongoing diffusion of hydrogen or iron. Therefore, a second material was added to work as a foundation, and which does not play a direct part in the redox process but minimizes or slows down the agglomeration and formation of the dense outer layer during redox cycles. The storage materials currently under investigation include ZrO_2, YSZ (yttria-stabilized zirconia), and CaO as a scaffold. A volume ratio of 70%/30% between iron oxide and the second material was taken as a compromise of high storage capacity and stable microstructure/cyclability.

The storage materials with different compositions were first characterized in a furnace under simulated gas conditions corresponding to charge and discharge environments during ROB operation. Selected compositions were then integrated into stacks for battery tests. Without complicated sealing or construction of the stacks and test benches, different storage compositions can be tested and characterized using the available stack design and test benches after only small modifications. The electrochemical characterization of the battery performance with Fe-based storage materials and conventional YSZ-based anode-supported fuel cell (ASC) stacks in a stagnant atmosphere will be presented.

2. Experiments

2.1. Battery configuration

Two-layer short stacks corresponding to the JÜLICH F10- design [11] were used for the battery tests. These stacks consist of thick interconnects made of Crofer 22 APU and ASCs based on 8YSZ, with an LSCF air electrode ($La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$) and screen printed GDC ($Ce_{0.8}Gd_{0.2}O_{1.9}$) diffusion barrier layer. The GDC layers of all ASCs for ROB tests were sintered at 1250 °C, and it was proven later that the cell performance was poorer than the standard ones sintered at higher temperatures [12]. The ASCs have an outer dimension of 10 cm × 10 cm, while the area of the active electrode is ~80 cm^2. The air side of the interconnects was coated against Cr-evaporation with an MnO_x protective layer by means of wet powder spraying (WPS). A nickel mesh was welded onto the fuel side of the interconnect to serve as the electrical contact. Before welding, tape cast storage components were placed in the milled channels after sintering. For this purpose, thick interconnects of 5.5 mm instead of 2 mm were used, into the fuel side of which 17 channels (~$90 \times 6 \times 2$ mm^3) for the storage materials were milled. The depth of the channels was later increased to 3 mm for a higher storage capacity. Depending on the compositions and preparation methods of the storage materials, as well as the depth of the channels, each interconnect contained up to 60 g in storage (i.e. ~0.5 mol Fe). Glass-ceramic was applied by dispenser to enable bonding inside the stack. Shaped mica gaskets were used as flat sealing between the stack and adaptor plate in the furnace.

2.2. Novel testing concept

During ROB tests, the stacks/batteries were tested with a stagnant atmosphere on the fuel side, which is a crucial requirement for characterization of the storage materials in the stack environment. In principle, the stagnant atmosphere can be obtained by simply closing the gas inlet and outlet. However, due to the unavoidable leakages (even tiny ones) from the stack, periphery of the test bench and interfaces in-between, it is difficult to keep the gas composition stable over time. Therefore, the test bench was modified for ROB tests. As shown in Fig. 1, an H_2 bypass was connected from an H_2 inlet to exhaust gas through a mass flow controller (MFC) and a small capillary tube. During ROB tests, the valve on the fuel outlet side (A) must be closed. All other gases except the H_2 bypass are also closed (valves B, C, D are open). A