Development of storage materials for high-temperature rechargeable oxide batteries

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ABSTRACT

A high-temperature rechargeable oxide battery (ROB) comprises a regenerative solid oxide cell (SOC) and oxygen-ion storage that consists of a porous Fe_2O_3 base redox material. This material possesses good redox kinetics, a high oxygen-ion storage capacity, and an acceptable long-term stability. Yet, observations demonstrate degradation effects such as particle coarsening and an outward diffusion of iron leading to layer formation during operation of the ROB at 800 °C.

To clarify the influence of the material composition on degradation, various oxides were added as a stabilizing scaffold for the Fe_2O_3 base material. Pressed samples of the binary mixtures were sintered in air at 900 °C and subsequently redox-treated up to 20 times under conditions that simulate those present in an actual ROB (800 °C, Ar–2%H_2 or Ar–7%H_2O–2%H_2). Afterwards, the degradation properties were analyzed by laser microscopy and the phase composition was measured using X-ray diffraction. Results indicate that the addition of yttria-stabilized zirconia (8YSZ) or pure zirconia (ZrO_2) can suppress structural degradation thus maintaining reaction kinetics. In contrast, the use of yttria (Y_2O_3) does not significantly mitigate degradation phenomena. Consequently, storage components consisting of 8YSZ and Fe_2O_3 were employed in an ROB test, resulting in more than 200 cycles with a current density of 150 mA/cm^2 and cycle durations of up to 70 min.

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1. Introduction

Energy storage will be essential in the future energy grid because of an increasing amount of renewable power sources and thus a large discrepancy between installed (rated) power and actual power input. Today, the largest share of the surplus grid energy is stored by pumped hydroelectric storage (PHS) plants with a high round-trip efficiency (≈80%) and a large capacity. Currently, PHS represents almost 99% of the worldwide electricity storage capacity [1]. Although there is still large potential for an increase in overall capacity, the expansion and the new construction of this type of storage are often limited by topographic, geological, and socio-economic factors. Hence, electrochemical storage is also being installed, albeit on a much smaller scale, in order to locally increase electricity storage capacity as well as to provide control power (regulating power) for grid services.

Several different electricity storage devices are in use or under development to meet the requirements for the stationary storage of electricity. These are namely a high capacity, a high round-trip efficiency, a long lifetime, quick response times, low life-cycle cost, and low environmental impact. These storage systems include mainly lead-acid batteries and increasingly also lithium-ion batteries as well as so-called flow batteries [2,3]. Yet, these devices are still quite expensive, may be limited in basic materials resources, provide a relatively low specific capacity, and might not meet safety regulations.

For storing larger amounts of energy electrochemically, water may be split into oxygen and hydrogen using an electrolyzer. Subsequently, the electrolytically generated hydrogen can either be directly used as fuel, e.g. hydrogen-fed passenger cars or be employed in the synthesis of methane to be stored for further use in the gas grid (power-to-gas, P2G) or for the production of methanol as an alternative fuel (power-to-fuel, P2F). As these processes involve handling and storing hydrogen and multiple steps during further synthesis, safety and also cost are a major concern. In this context, the relatively new concept of a
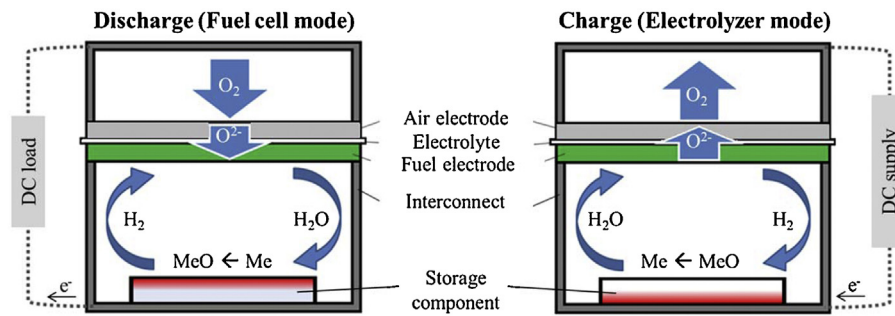
Fig. 1. Schematic showing the working principle of a rechargeable oxide battery (ROB) according to [5]. Discharging: oxidation of metal; charging: reduction of metal oxide.

rechargeable oxide battery (ROB) has been proposed by several authors [4–7] because cost can be reduced and safety be increased.
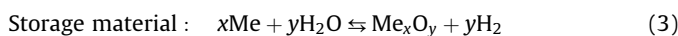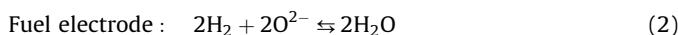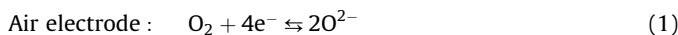
The main efforts in developing this novel battery type are to increase the current density (currently: 150 mA/cm^2) and to limit the degradation of the integrated storage components thus ensuring good performance and long battery life. Therefore, the present study describes the development of an optimized storage material to be applied inside the ROB. Firstly, the working principle and the prevailing conditions of the ROB are presented. Then, the material preparation and analysis methods are explained, followed by the description of actual ROB tests. After presentation and discussion of the results, the highlights are summarized in the conclusion.

1.1. Working principle of a rechargeable oxide battery

The ROB consists of a reversible solid oxide cell (SOC) and a porous oxygen-ion storage material. Both components are coupled by a gaseous H$_2$–H$_2$O medium acting as a carrier of oxygen ions. The working principle of the new rechargeable battery is depicted in Fig. 1.

During ROB discharge (fuel cell mode), atmospheric oxygen is catalytically reduced at the air electrode yielding oxygen ions. These ions diffuse through the ceramic electrolyte (8YSZ, with 8 mol% yttria-stabilized zirconia) and oxidize hydrogen at the fuel electrode, thereby forming steam and releasing electrons. The generated steam then oxidizes the metal in the storage component, thereby releasing further hydrogen for ongoing electricity generation.

During charging, steam is electrolyzed at the fuel electrode generating hydrogen. The hydrogen is used to reduce the metal oxide and the thus produced steam is used during the ongoing electrolysis. Accordingly, three electrochemical reactions proceed simultaneously in the ROB. The first reactions (Eqs. (1)–(2)) are known to take place within a fuel cell or an electrolyzer at the respective electrodes. Eq. (3) denotes the reaction of the gas with the storage material.

$$\text{Air electrode}: \quad O_2 + 4e^- \leftrightarrows 2O^{2-} \tag{1}$$

$$\text{Fuel electrode}: \quad 2H_2 + 2O^{2-} \leftrightarrows 2H_2O \tag{2}$$

$$\text{Storage material}: \quad xMe + yH_2O \leftrightarrows Me_xO_y + yH_2 \tag{3}$$

1.2. Operating conditions

Conventional reversible SOC systems are usually operated at temperatures between 700 °C and 800 °C. The elevated temperatures are necessary to achieve sufficiently high oxygen-ion conductivity of the thin (5–10 μm) ceramic 8YSZ electrolyte

[8]. At the same time, the gas mixture within the fuel compartment of the SOC is composed of 20% H$_2$O and 80% H$_2$ (H$_2$O/H$_2$ = 1/4) in fuel cell mode and 80% H$_2$O and 20% H$_2$ (H$_2$O/H$_2$ = 4/1) in electrolyzer mode. These atmospheres ensure that nickel, which is the catalyst in the fuel electrode, always prevails in metallic form. Likewise, chromia (Cr$_2$O$_3$) maintains its oxide state, which is necessary in order to fulfill its function as a part of the protective and conductive layer of the ferritic steel interconnect in the SOC stack [9]. At 800 °C, the mentioned H$_2$O/H$_2$ ratios correspond to oxygen partial pressures (p_{O_2}) of 2.8×10^{-20} bar (fuel cell mode) and 7.0×10^{-18} bar (electrolyzer mode), respectively (Fig. 2).

In an ROB, the atmosphere is stagnant. Yet, the prevailing gas compositions and the oxygen partial pressures are similar to those in an SOC. The storage material in an ROB must be oxidizable at the upper end (H$_2$O/H$_2$ = 4/1, $p_{O_2} = 7.0 \times 10^{-18}$ bar) of the mentioned range of oxygen partial pressures. Likewise, it must be reducible at the lower end (H$_2$O/H$_2$ = 1/4, $p_{O_2} = 2.8 \times 10^{-20}$ bar). A number of metal-metal oxide systems fulfill this requirement and might thus be applied as storage materials. Considering the thermodynamic stabilities, the metal-metal oxide systems based on germanium, tungsten, molybdenum, and iron are potentially suitable candidates, depending on the exact range of oxygen partial pressure [11]. However, due to the drawbacks of tungsten and molybdenum, which form highly volatile or even liquid oxides at around 800 °C, and the quite high cost of germanium, the present investigation focuses on iron base storage components.

Iron is cheap, widely available and environmentally friendly. Moreover, as indicated in Fig. 2, the dissociation pressures ($p_{O_2,dis}$) of the iron oxides wustite (FeO) and magnetite (Fe$_3$O$_4$) lie well within the relevant operation window of the battery
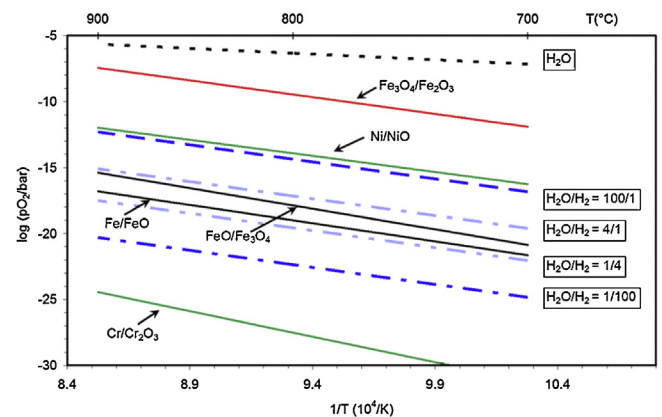

Fig. 2. Equilibrium oxygen partial pressures (dashed lines) in various H$_2$O/H$_2$ mixtures and in pure steam as a function of reciprocal temperature compared with data on the dissociation pressures of selected oxides (solid lines); calculated with Fact Sage [10].