



Degradation of ferritic stainless steels under conditions used for solid oxide fuel cells and electrolyzers at varying oxygen pressures



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ABSTRACT

Four commercial ferritic stainless steels were tested at 850 °C in oxygen pressures ranging from 10⁻⁴ to 1 atm, in order to investigate the isolated effect of oxygen pressure on corrosion, in the context of solid oxide electrolysis cells. The oxidation rates of all steels were essentially independent of oxygen partial pressure, which indicates n-type behavior. FIB/SEM analysis revealed that the grain size of the oxides was found to decrease at lower oxygen pressures. Volatile Cr species evaporation in pure oxygen was significantly lower than what has been reported for simulated solid oxide fuel cell environments with humid air.

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1. Introduction

Solid oxide fuel cells (SOFCs) are able to convert chemical energy from fuels directly into electricity with high efficiency and without combustion. Due to the high operating temperature other fuels in addition to pure hydrogen, such as natural gas, can be used. This makes them suitable for applications such as combined heat and power units in households [1] and auxiliary power units in trucks [2], but they are also considered for power plant scale electricity production [3,4]. Moreover, SOFCs can run in reverse mode, i.e. to electrolyze steam into hydrogen by feeding water and electric current to produce hydrogen and oxygen, and are then referred to as solid oxide electrolysis cells (SOEC). The high operating temperature gives SOECs exceptionally high efficiencies and the ability to electrolyze carbon dioxide into carbon monoxide, which in combination with water electrolysis makes syngas production possible [5,6]. But a common challenge for both SOFC and SOEC technology is to increase operating lifetime with sufficiently low cost materials. The cost of material degradation have been pointed out as one of the main contributors to the hydrogen price for electrolyzed H₂ production [7].

In order to increase power density, individual cells are interlinked to form a stack of cells. Interconnects are components that provide electrical contact between adjacent cells and separate and distribute the fuel and oxidant gases [8,9]. In planar stacks, the

interconnects make up a large part of the total material used and are thus a considerable cost [10]. The most commonly considered materials for interconnects are ferritic stainless steels due to their desirable properties, such as matching thermal expansion coefficient (TEC) with other cell components, ease of fabrication, high thermal and electrical conductivity and the formation of oxide products with an acceptably low electrical resistance, i.e. chromium oxide [11]. The buildup of oxide products, or corrosion, is one of the main material issues with metallic interconnects. Both anode and cathode environments in SOFC and SOEC stacks causes ferritic stainless steels to oxidize. During operation a Cr₂O₃ scale continuously grows on the substrate surface, resulting in a steady increase in electrical resistance [12–14]. Eventually, the increased oxide thickness will lead to spalling of the oxide scale and consequently lost electrical contact between electrodes and interconnects [15]. Another challenge with chromia-forming interconnects is to reduce chromium evaporation and the consequent poisoning of electrodes [16,17]. Several coating solutions have been developed that minimize chromium evaporation and slow down oxidation [13]. These include different spinel and perovskite cap layers as well as the addition of reactive elements such as yttrium, cerium or hafnium [13,18,19].

Studies that have investigated degradation in simulated fuel electrode and oxygen/air electrode environments have led to discrepancies in whether oxidation is slower, faster or unchanged [11,20]. The oxidation mechanisms in fuel and oxygen environments are often discussed in terms of oxygen partial pressure since the concentration of oxygen at the fuel electrode is several orders of magnitude lower than at the oxygen electrode. Palcut et al. studied ferritic stainless steels with chromium contents of 20–29% in dry

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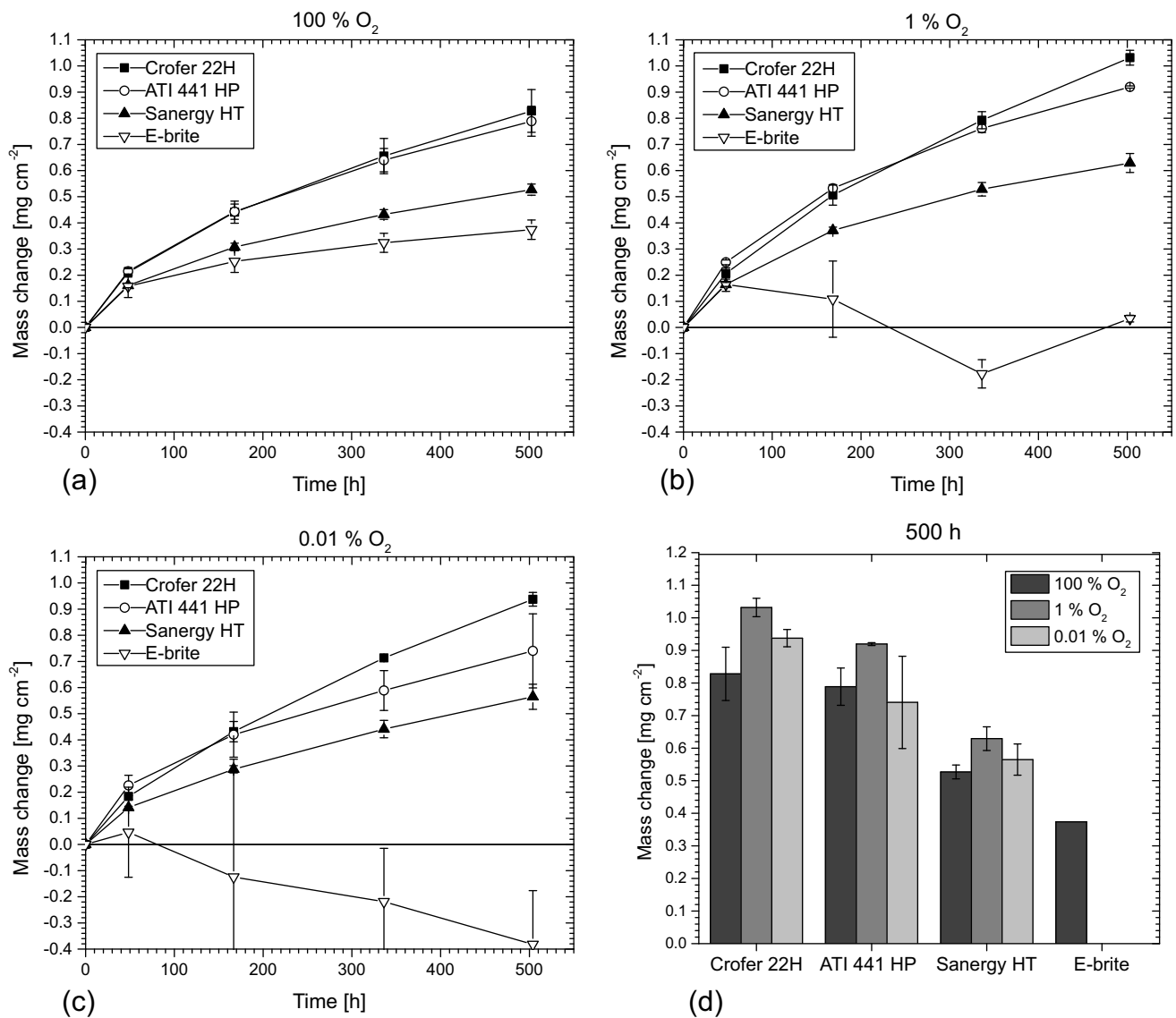


Fig. 1. Oxidation kinetics for Sanergy HT, Crofer 22H, E-Brite and 441HP in (a) 100% O₂ (b) 1% O₂ and (c) 0.01% O₂. The mass gain after 500 h for all four ferritic stainless steels is summarized in (d) but the negative mass change for E-brite has been omitted. The average mass from repeated exposures is plotted for the respective test atmospheres and the standard deviation is represented by the error bars.

oxygen, humidified air and humidified hydrogen [21]. They found that the oxidation rate was faster in air and oxygen than in wet hydrogen and concluded that this was due to the increase in oxygen pressure. In contrast, in a study by Ardigo et al., a higher oxidation rate was observed in a simulated fuel electrode environment than in an oxygen electrode environment for the 18% Cr steel AISI 441 [22]. When a higher alloyed steel, Alloy 230, was exposed in the same environments the opposite relation was found in Ref. [23]. In addition, Kurokawa et al. exposed SUS430, a 16% Cr steel, in humid hydrogen and air and did not see any difference in oxidation rate as a function of oxygen pressure [24].

When oxygen partial pressure is discussed, the environments used for low oxygen partial pressures are often generated by mixtures of H₂/H₂O or CO/CO₂. Yet, water, as a reactant itself, has been shown to affect the oxidation behavior of chromia-forming alloys [25–28]. Hydrogen has also been shown to have effects on oxidation [29]. Therefore, the aim of this study is to examine the isolated effect of oxygen pressure on the corrosion of fer-

ritic chromia-forming interconnect steels. The goal was also to obtain fundamental insights into the potential consequences if SOFC stacks are run in SOEC mode. Furthermore, some studies have also shown that operation at elevated pressures, which means higher oxygen concentration, could lead to overall system benefits [30–32]. In this study, the degradation of four commercial ferritic stainless steels was investigated in oxygen pressures ranging from 10⁻⁴ to 1 atm at 850 °C. Oxidation kinetics, oxide scale evolution and microstructure were investigated and additionally measurements of the evaporation of volatile chromium species were carried out.

2. Experimental

2.1. Sample preparation

The materials studied were Sanergy HT (Sandvik), Crofer[®] 22 H (ThyssenKrupp), E-Brite[®] (ATI) and ATI 441HP[™] (ATI), all of them

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