

# A combined SEM and CV study of solid oxide fuel cell interconnect steels

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Received: 1 May 2011 / Revised: 23 August 2011 / Accepted: 24 August 2011 / Published online: 6 September 2011  
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**Abstract** Scanning electron microscopy and cyclic voltammetry were used to investigate the high-temperature oxidation behavior of two solid oxide fuel cell interconnect steels. One alloy had a low content of manganese; the other alloy had a high content of manganese. Four reduction and four oxidation peaks were observed in the voltammograms of the low manganese alloy at a temperature of 800 °C. The voltammograms of the alloy with a high content of manganese were different. At 600 °C, three reduction peaks and two oxidation peaks were observed. At 800 °C, additional peaks were observed in the voltammogram for this alloy.

## Introduction

A solid oxide fuel cell (SOFC) is a high-temperature electrochemical device that converts chemical energy into heat and electricity [1]. To obtain a sufficient voltage, the cells are stacked [2]. In order to do this, interconnects are needed. If a lowering of the operation temperature, from approx. 800 to approx. 600 °C, of the SOFC can be achieved, then low-cost interconnect FeCr alloys (stainless steels) can be used instead of expensive ceramic interconnects. Consequently, FeCr alloys have been the subject of numerous oxidation studies for the potential use as interconnect materials in a SOFC stack, see i.e., [3] for a review.

**Electronic supplementary material** The online version of this article (doi:10.1007/s10008-011-1542-1) contains supplementary material, which is available to authorized users.

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High-temperature cyclic voltammetry (CV) is a technique that can be used to study the reduction and formation of oxides on alloys [4]. The idea behind the use of CV is that the potential applied to the working electrode (i.e., the alloy) is coupled to the oxygen partial pressure at the working electrode/electrolyte interface through the Nernst equation. That means that the oxygen partial pressure, felt by the working electrode, can be varied. CV can then answer which oxides will be present on the surface of the alloy as a function of the partial pressure of oxygen. CV can also predict whatever the oxidation/reduction proceeds in one or more steps. Only a few examples of the use of this technique to study the oxidation of alloys have been given in literature [5].

In this work, the products of oxidation on two different FeCr alloys have been studied by the use of high-temperature CV, together with scanning electron microscopy (SEM).

One alloy had a low content of manganese, the other a high content of manganese. The aim of this study was to study the effect of manganese on the high-temperature oxidation processes of FeCr alloys, with high-temperature CV and SEM.

## Experimental

The compositions of the two alloys are given in Table 1. It is seen that the Crofer 22 APU alloy (Krupp–Thyssen) contains a small amount of manganese, whereas the 434 alloy (Sandvik) contains a large amount of manganese. In addition to the elements given in Table 1, the alloys contain small amounts of other elements. For the SEM study, the alloys were oxidized at 600 or 800 °C for 250 h in air. The micrographs were recorded with a Jeol JSM-5310LV low vacuum scanning electron microscope (LV-SEM). The LV-

**Table 1** The main compositions of the two alloys

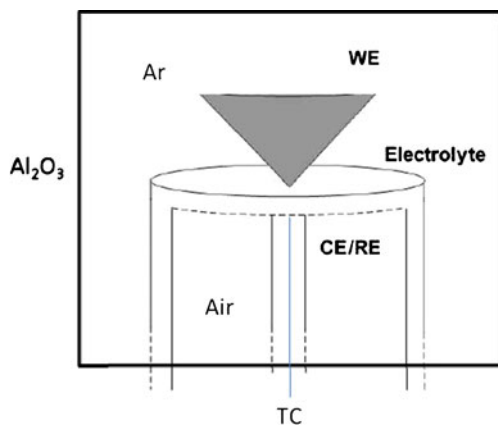
Sample designation	wt.% Fe	wt.% Cr	wt.% Mn	wt.% Si
Crofer 22APU	Bal.	22.9	0.5	0.02
Sandvik 434	Bal.	22.2	5.1	0.14

The alloys also containing small amounts of C, Ce, Al, La and Ti

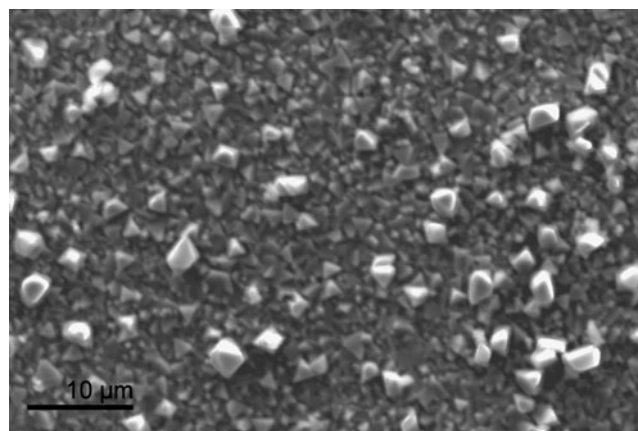
SEM was equipped with an energy dispersive (EDS) detector. Only the surfaces of the oxidized alloys were investigated. The SEM/EDS were done at room temperature. The samples were cooled in air with a rate of 100 °C/h.

The experimental setup for the CV studies is shown in Fig. 1. The setup is a two atmosphere setup, with separate gasses for working and counter/reference electrodes. As an electrolyte, a one-end closed yttria-stabilized zirconia (YSZ, Vesuvius) tube was used. The closed end of the YSZ tube, exposed to the working electrode, was polished with 1- $\mu\text{m}$  diamond paste before use. The counter/reference electrode was added, in the form of platinum paste (Engelhard), to inside of the YSZ tube. After adding the platinum paste, the platinum electrode was heat-treated at 1,000 °C for 2 h. The size of the counter/reference electrode is approximately 0.5 cm<sup>2</sup>. The inside of the YSZ tube contained air (with a fixed oxygen partial pressure). Electrical connection to the counter/reference electrode was done with a Pt/PtRh thermocouple.

Sheets of the alloys were laser-cut into triangles, with the dimensions 27.5×14×0.2 mm. The tip of the triangle was then pushed towards the YSZ electrolyte with approximately 60 g of weight. This gives a contact area of less than 10<sup>-3</sup> cm<sup>2</sup>.



**Fig. 1** The experimental setup used for the cyclic voltammetry studies. The setup is a two-atmosphere setup (air and argon). The working electrode (WE) is the FeCr-based alloy, the reference electrode/counter electrode (RE/CE) is a Pt electrode, and the electrolyte is a one-end closed YSZ tube. The RE/CE is placed in contact with the YSZ tube, inside the YSZ tube. Contact to the RE/CE is done by a thermocouple (TC). The inside of the YSZ tube contains air. The surrounding Al<sub>2</sub>O<sub>3</sub> tube contains Ar during the measurements

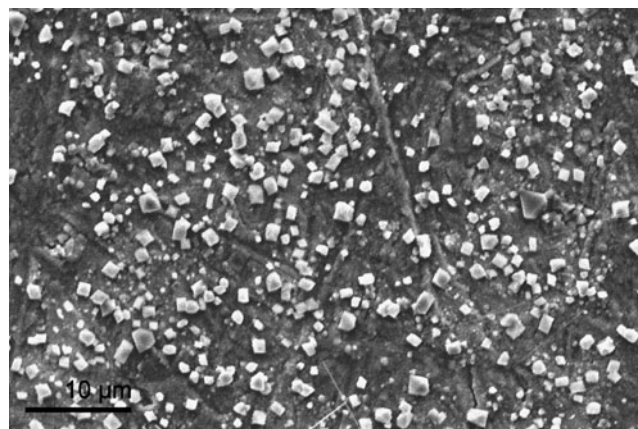


**Fig. 2** A micrograph of the surface of the Crofer alloy after oxidation at 800 °C for 250 h in air. The oxide scale formed on the surface of the alloy contains Cr-, Mn-, and Fe-based oxides

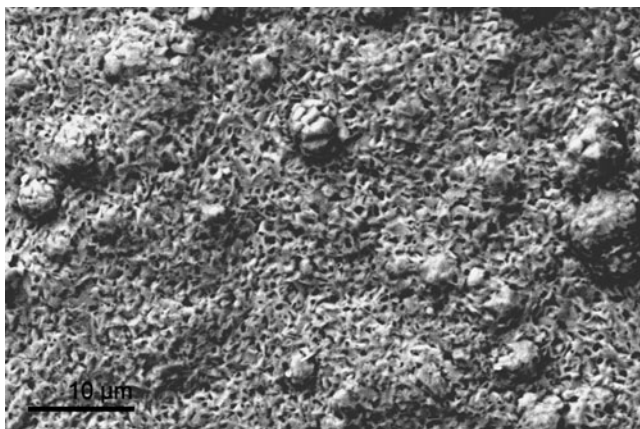
The setup is a pseudo three-electrode setup. The size of the counter/reference electrode is many times larger than the working electrode, so the counter/reference electrode will only be polarized to a very little extent when recording the voltammograms.

The alloys were heated in air to the temperatures of 600 or 800 °C, before recording the voltammograms. The alloys were oxidized for 24 h in air before the measurements, while the samples were in contact with the electrolyte. Electrical connection to the working electrode was done with a gold wire.

For recording the voltammograms, a THJ Instruments POT100 potentiostat was used. The sensitivity of the potentiostat is in the nA range. The voltammograms were recorded in the potential window 0.3 to -2.0 V vs. Pt | air. The voltammograms were recorded in an argon atmosphere (the working electrode chamber contained Ar). Sweep rates of 100, 10, and 1 mV/s were used. The alloys were equilibrated at anodic potentials (0.3 V vs. air) before the



**Fig. 3** A micrograph of the surface of the 434 alloy after oxidation at 600 °C for 250 h in air. The isolated crystals are Si- and Mn-rich oxides



**Fig. 4** A micrograph of the surface of the 434 alloy after oxidation at 800 °C for 250 h in air. The oxide scale formed on the surface of the alloy contains Cr, Mn, and traces of Fe-based oxides

recording of the voltammograms. The gas was changed from air to Ar while the samples were polarized. The gas change took approximately 1 h.

**Results**

A selection of SEM micrographs can be found in Figs. 2, 3, and 4. In Fig. 2, the micrograph of Crofer heat-treated at 800 °C for 250 h in air can be found. Results of the EDS point scan analysis shows that the oxidized surface contains oxides of chromium, iron, and manganese, see Table 2. The SEM micrographs of the manganese-rich 434 alloy heat-treated at 600 °C for 250 h in air show that the surface of the oxidized alloys contains small isolated crystals, see Fig. 3. The EDS point analysis shows that these crystals contain manganese. The surface not containing the isolated crystals contains oxides of silicium, chromium, manganese, and traces of iron, see Table 2. For the same alloy heat-treated at 800 °C in air, a markedly different surface topography is observed, with a more smooth oxide scale, see Fig. 4. This oxide scale contains mainly chromium and manganese with traces of iron.

An example of a voltammogram for Crofer recorded at 800 °C can be seen in Fig. 5. It is seen that the voltammogram contain four oxidation and four reduction

peaks. The Crofer alloy oxidized at 600 °C shows a similar behavior to the one observed at 800 °C.

Voltammograms from the Sandvik 434 alloy at temperatures of 600 and 800 °C can be found in Figs. 6 and 7. The behavior of this alloy is markedly different from the behavior of the Crofer alloy. At 600 °C, only three reduction and two oxidation peaks are observed. Spikes are observed in connection with the second reduction peak. At 800 °C, three to four reduction peaks are observed. Five oxidation peaks are observed in the voltammogram.

**Discussion**

The standard potentials for the formed oxides can be calculated using the equation:

$$E^0 = - \Delta G^0 / nF \tag{1}$$

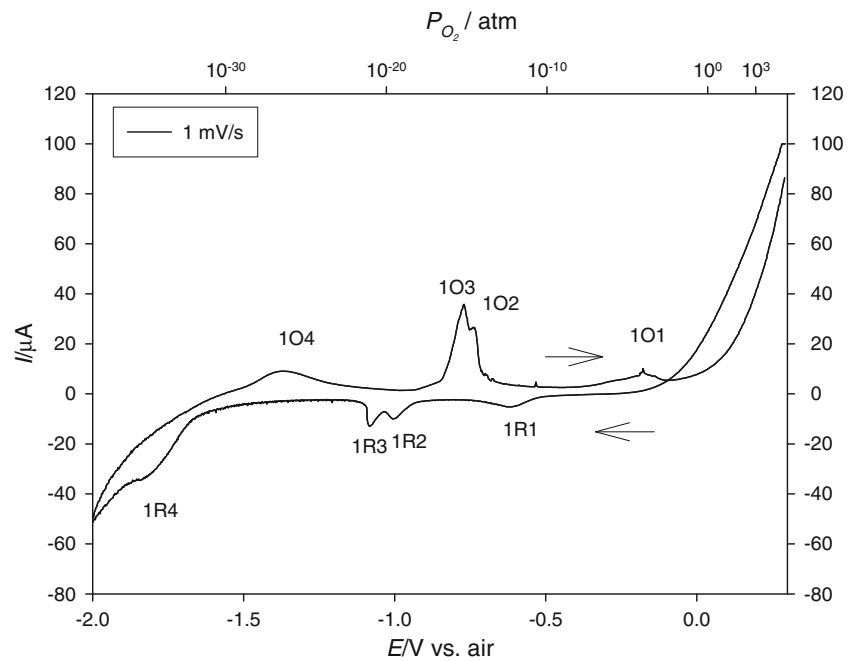
$\Delta G^0$  is the change in Gibbs free energy,  $n$  is the number of electrons, and  $F$  is Faraday's number. The calculated potentials are given in Table 3 at 600 and 800 °C, respectively. The  $\Delta G^0$  values, used for the calculations of the standard potentials of the formed oxides, were calculated using the program FactSage [6].

The information found in Table 3 can be used to assign the peaks in the voltammograms to specific redox reactions. In determining the redox reactions attributed to the different peaks, the onsets of the peaks were used to determine the  $E_0$  values. From the voltammogram recorded on Crofer at 800 °C, the following can be deduced. The reduction of Fe-oxides occurs in three steps. First,  $Fe_2O_3$  (hematite) is reduced to  $Fe_3O_4$  (magnetite) (1R1,  $-0.53$  V vs. air), the first reduction peak. This reaction was picked instead of the reduction of  $Mn_3O_4$  to  $MnO$  as no other indications of redox-active manganese are visible in the voltammograms.  $Fe_3O_4$  is then reduced to  $FeO$  (wüstite) (1R2,  $-0.92$  V vs. air), which is stable in only a narrow oxygen partial pressure window. The last step in the reduction of Fe-oxide is the reduction of  $FeO$  to elemental Fe (1R3,  $-1.03$  V vs. air). The last peak in the reduction process is the reduction of  $Cr_2O_3$  to Cr (1R4,  $-1.67$  V vs. air). In contrast to the reduction of Fe-oxide, the reduction of  $Cr_2O_3$  to Cr is a one-step process. The oxidation of Cr and Fe occurs in the reverse

**Table 2** The compositions of the oxidized alloys in percent

	Crofer, 800 °C		434, 600 °C		434, 800 °C
	Background	Crystals	Background	Crystals	800 °C
Si	–	–	75	63	–
Cr	60	57	14	11	16
Mn	28	23	7	22	82
Fe	12	20	4	4	2

**Fig. 5** A voltammogram recorded on Crofer at 800 °C in argon, after exposure to air for approximately 24 h. Four reduction and four oxidation peaks are observed. The peaks are named 1R1 to 1R4 and 1O1 to 1O4. *R* is a reduction peak and *O* is an oxidation peak. See text for explanation of processes assigned to the peaks. Legend is sweep rate

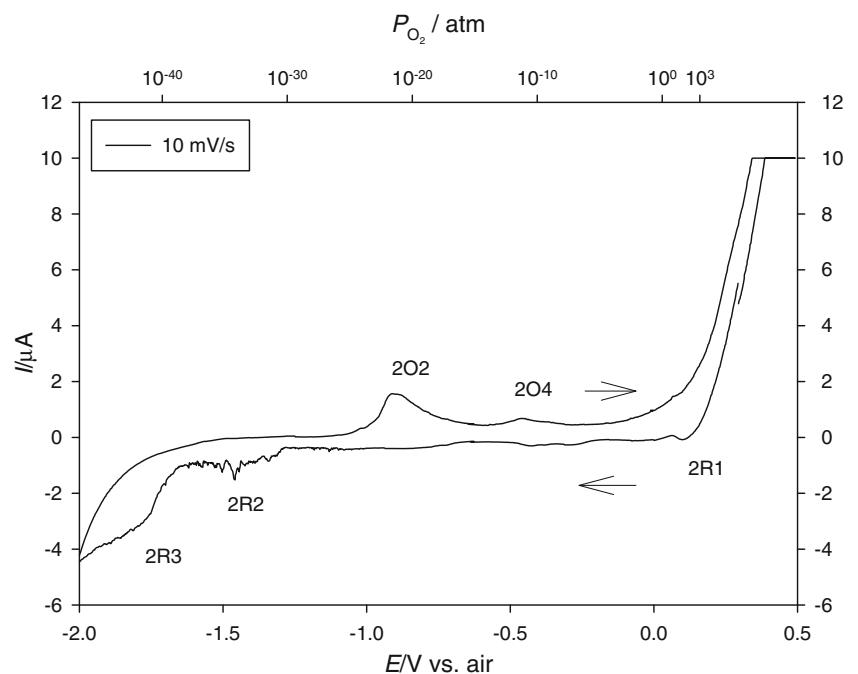


order of the reduction reactions, that is Cr is oxidized in one step (1O4,  $-1.4$  V vs. air) and Fe is oxidized in three steps (1O3,  $-0.84$  V vs. air, 1O2,  $-0.74$  V vs. air, and 1O1,  $-0.3$  V vs. air). No signs of redox-active Mn oxides are observed in the voltammograms. This is likely because the amount of Mn oxides in the surface of the oxidized alloy is below the detection limit of the CV technique. However, EDS point analysis recorded on the Crofer alloy heat-treated at 800 °C for 250 h shows sign of mainly

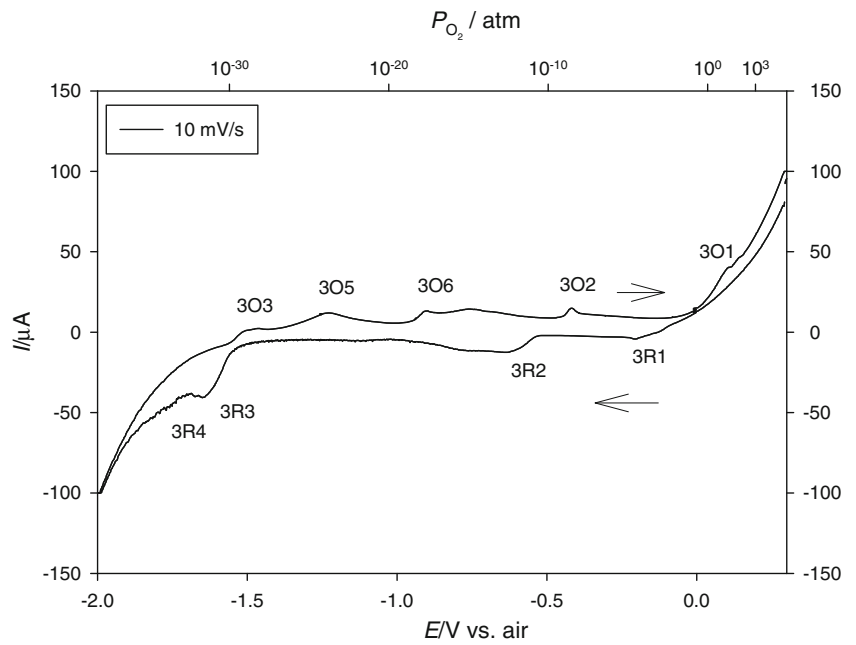
manganese and chromium in the surface. This point in the direction that the oxide scale formed first on the surface is iron rich. After longer time at elevated temperature, manganese-based oxides then start to form on the surface.

The oxidation process of the Sandvik 434 alloy with 5 wt.% Mn is quite different. At 600 °C, three reduction peaks are observed. This first peak (2R1, 0.1 V vs. air) corresponds well with the calculated potential for the reduction of  $\text{MnO}_2$  to  $\text{Mn}_2\text{O}_3$ . The second reduction peak is the

**Fig. 6** A voltammogram recorded on 434 at 600 °C in Ar. Three reduction and two oxidation peaks are observed in the voltammogram. The peaks are named 2R1 to 2R3 and 2O2 and 2O4. *R* is a reduction peak and *O* is an oxidation peak. See text for explanation of processes assigned to the peaks. Some weak and broad peaks can also be seen in the voltammogram. Legend is sweep rate



**Fig. 7** A voltammogram recorded on 434 at 800 °C in Ar. Four reduction and five oxidation peaks are observed in the voltammogram. The peaks are named 3R1 to 3R4 and 3O1, 3O2, 3O3, 3O5, 3O6. R is a reduction peak and O is an oxidation peak. See text for explanation of processes assigned to the peaks. Legend is sweep rate



reduction of  $Mn_2O_3$  to elemental Mn (2R2,  $-1.3$  V vs. air). That only redox-active manganese-based oxides are observed in the voltammograms corresponds well with the SEM study that shows crystals of manganese oxide in the surface of the oxidized alloy. This explains why only the reduction of manganese oxide is observed in the voltammograms at a temperature of  $600$  °C, as the crystals of manganese oxides will be the only part of the oxidized alloy that is in contact with the electrolyte. It might also be that the reduction of the other types of oxide in the surface are very slow at  $600$  °C, and therefore not revealed in the voltammograms.. Some very weak and broad peaks are

observed in the voltammogram (around  $-0.5$  V vs. Pt | air). This could be due to small amounts of Fe oxide. A peak from the reduction of  $Cr_2O_3$  to elemental Cr is also observed at a lower potential in the voltammogram (2R3,  $-1.67$  V vs. air). A large offset is observed for this reaction in contrast to the case of Crofer at  $800$  °C. This could be due to slow kinetics at  $600$  °C compared to  $800$  °C. Upon reversal of the scan direction, two oxidation peaks are observed. The first peak (2O2,  $-0.98$  V vs. air) is either oxidation of Fe to FeO or  $Fe_3O_4$  (most likely) or Mn to  $Mn_3O_4$  or  $Mn_2O_3$ . The second peak is the oxidation of  $Fe_3O_4$  to  $Fe_2O_3$  (2O4,  $-0.52$  V vs. air). No sign of formation of chromium

**Table 3** Calculated standard free energy  $\Delta G^0$  and E vs. air in V at 600 and 800 °C

Reactions	$\Delta G^0$ (600 °C)	E (600 °C)	$\Delta G^0$ (800 °C)	E (800 °C)
$Mn+0.5 O_2 \rightleftharpoons MnO$	-315.2	-1.60	-299.3	-1.51
$2Mn+1.5 O_2 \rightleftharpoons Mn_2O_3$	-714.2	-1.20	-659.4	-1.10
$3Mn+2 O_2 \rightleftharpoons Mn_3O_4$	-1 060.0	-1.34	-986.1	-1.24
$3MnO+0.5 O_2 \rightleftharpoons Mn_3O_4$	-114.5	-0.56	-88.2	-0.42
$2Mn_3O_4+0.5 O_2 \rightleftharpoons 3Mn_2O_3$	-22.3	-0.086	-6.0	-0.0053
$Mn_2O_3+0.5 O_2 \rightleftharpoons 2MnO_2$	4.1	0.078	15.7	0.12
$Mn_3O_4+O_2 \rightleftharpoons 3MnO_2$	0.4	0.055	40.5	0.22
$Si+O_2 \rightleftharpoons SiO_2$	-741.1	-1.89	-703.5	-1.79
$2 Al+1.5 O_2 \rightleftharpoons Al_2O_3$	-1 385.1	-2.36	-1 316.1	-2.24
$2 Cr+1.5 O_2 \rightleftharpoons Cr_2O_3$	-881.5	-1.49	-828.0	-1.39
$Fe+0.5 O_2 \rightleftharpoons FeO$	-202.1	-1.01	-188.1	-0.93
$2 Fe+1.5 O_2 \rightleftharpoons Fe_2O_3$	-577.1	-0.98	-524.0	-0.86
$3 Fe+2 O_2 \rightleftharpoons Fe_3O_4$	-805.9	-1.01	-741.0	-0.92
$3 FeO+0.5 O_2 \rightleftharpoons Fe_3O_4$	-199.6	-1.00	-176.5	-0.88
$2 Fe_3O_4+0.5 O_2 \rightleftharpoons 3Fe_2O_3$	-119.6	-0.59	-90.1	-0.43

The standard free energy is given in kilojoule per mole (kJ/mol)

oxide is observed in the voltammogram. This could be because the oxidation of chromium is very slow at 600 °C.

At higher temperature, 800 °C, additional peaks are observed in the voltammograms. The first reduction peak can be assigned to the reduction of  $\text{Mn}_2\text{O}_3$  to  $\text{Mn}_3\text{O}_4$  (3R1,  $-0.16$  V vs. air). The second reduction peak is quite broad. This peak can be assigned to the reduction of  $\text{Fe}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_3$  to lower valent oxides of Fe and Mn (3R2,  $-0.54$  V vs. air). The third reduction peak is the reduction of the Cr(III) to Cr metal (3R3,  $-1.56$  V vs. air). A very weak reduction peak with some spikes is observed after this. This is the reduction of MnO to Mn metal (3R4,  $-1.71$  V vs. air). Several peaks are observed upon reversal of the scan direction. The first oxidation peak can be assigned to the oxidation of Mn metal to MnO (3O3,  $-1.52$  V vs. air). The second oxidation peak is the oxidation of chromium to Cr(III) oxide (3O5,  $-1.28$  V vs. air). The third oxidation peak is the oxidation of Fe metal to either FeO, to the  $\text{Fe}_3\text{O}_4$  spinel or to  $\text{Fe}_2\text{O}_3$  (3O6,  $-0.93$  V vs. air). A weak oxidation peak is observed after this (3O2,  $-0.46$  V vs. air). This could be the oxidation of either the  $\text{Fe}_3\text{O}_4$  spinel to  $\text{Fe}_2\text{O}_3$  or the oxidation of MnO to the  $\text{Mn}_3\text{O}_4$  spinel. The last oxidation peak is the oxidation of  $\text{Mn}_3\text{O}_4$  to  $\text{Mn}_2\text{O}_3$  (3O1,  $0.04$  V vs. air). This again shows that manganese is oxidized and reduced in several steps just like iron. The CV study also shows that the oxidation of Mn is not just the reverse of the reduction Mn oxides, as observed for Fe and Cr.

Comparison of the CV measurements at 600 and 800 °C shows that different oxides of manganese are formed at 600 and 800 °C when oxidizing the Sandvik 434 alloy.

The discussion shows that it is possible to get insight into which oxides that are formed or reduced initially on the surface of alloys by the use of CV. That is the reduction of oxides of chromium and iron are the reverse of the oxidation of chromium and iron, whereas the reduction of

oxides of manganese are not the opposite of the oxidation of manganese. Together with SEM, the reduction/oxidation behavior of the alloys can therefore be understood in more detail, than by using SEM alone.

## Conclusion

CV can be used to study the reduction or oxidation of alloys. Together with SEM, this can give insight into the redox properties and the stability interval of the oxides of these alloys. It has been shown by CV that chromium is oxidized in one step, whereas iron and manganese are oxidized in several steps. The reduction of oxides of iron and chromium is the reverse of the oxidation of elemental iron and chromium, whereas the reduction of oxides of manganese is different from the oxidation of elemental manganese. Different oxides of manganese are formed during oxidation at 600 or 800 °C on the Sandvik 434 alloy.

**Acknowledgments** The technical staff at the Fuel Cells and Solid-State Chemistry Division is thanked for help with the preparation of samples. Financial support from energinet.dk is gratefully acknowledged.

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