$MnCo_2O_4$ Preparation by Microwave-Assisted Route Synthesis (MARS) and the Effect of Carbon Admixture

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Catalyst spinel $MnCo_2O_4$ with particle size <30 nm was prepared by a novel microwave-assisted route. To determine the optimal amount of carbon needed as a microwave susceptor, varying amounts of amorphous carbon powder (7−26 wt %) were mixed with the aqueous solutions of Mn- and Co-nitrates. After heat treatment at 200 °C in a conventional oven, the mixtures were heat-treated in a microwave oven (2.45 GHz) at a power of 350 W. The effect of the carbon amount on the formation and properties of the catalysts was studied. In this production method, 13 wt % of carbon was found to be the minimum needed for spinel $MnCo_2O_4$ formation. Most of the carbon was oxidized during the microwave treatment. When the carbon content in the nitrate−carbon mixture was increased beyond 13 wt %, the carbon content and the specific surface area of the final catalyst started to decrease. However, the carbon amount of 18 wt % in the initial nitrate−carbon mixture was found to be the most preferable when considering the catalytic activity of the spinel toward oxygen reduction reaction in alkaline electrolyte.

Introduction

Fuel cells are promising power sources for electronic devices and cars because of their friendliness to the environment and high electric efficiency. In a typical fuel cell, gaseous fuels and oxidants are fed continuously to the electrodes where oxidation and reduction reactions take place to produce an electric current. The electrode materials, especially the catalysts for the low- and intermediate-temperature fuel cells, must have high surface areas and small particle sizes, high porosity, and stable chemical structures to exhibit high rates of oxidation or reduction reactions.

In alkaline fuel cells (AFC) carbon can be used both as a catalyst together with another active catalyst for the oxygen reduction reaction (ORR), and as a support for the active catalyst. Carbon reduces oxygen into peroxide,[1] which the other catalyst further reduces into OH^-.[2] Further, carbon can be used to increase the dispersion of the catalysts and the surface areas, and improve the overall surface conductivity and accessibility of the reactants and electrolytes. The properties of carbon materials together with the catalysts, mode of preparation, and further incorporation in the electrode structure are all of primary importance.[3,4] Therefore, the synergetic effects of both the preliminary oxygen reduction into peroxide and incorporation of optimized catalysts have to be taken into account in order to operate AFC cathode gas-diffusion electrodes at substantial current densities and endurance tests. The selection of inexpensive catalysts for the ORR in AFC, compared to the expensive platinum group metals commonly used in acid-based fuel cells, is wide. Catalysts such as transition metal macrocycles, silver, and some metal oxides supported on high-surface-area carbons have been reported to show high activities for ORR.

The synthesis method has a significant effect on the physicochemical and electrochemical properties of a catalyst. Among various synthesis methods to produce porous metal oxide catalysts are, for instance, decomposition of salts, combustion, sol−gel, and spray pyrolysis.[5] For the rapid and energy-saving preparation of catalysts, microwave-assisted routes can be used. The ability of any material to absorb microwave energy is expressed by its dielectric loss factor combined with the dielectric constant.[6,7] The dielectric loss factor depends on the material, frequency, and temperature. Some metal nitrates have quite a high dielectric loss factor so that they can be decomposed in a dielectric field to produce metal oxides; for example, $La_{0.7}Ba_{0.3}MnO_3$ at 800 W,[8] $LaNiO_3$ at 700 W,[9] and zinc oxide varistors at

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600 W[10] with a frequency of 2.45 GHz. However, when a secondary heater is needed, the use of carbon is one option. For instance, graphitic carbon mixed with the precursor oxides has been used as a secondary heater in microwave-assisted synthesis of $LaCrO_3$[9] and oxides of Mo, Cr, and V.[11] Similarly, amorphous carbon as a microwave susceptor has been used in the preparation of transition metal silicides from the metallic precursors,[12] and in carbothermal reduction of metal oxides to produce metal nitrides.[13] Increasing the amount of carbon has been reported to increase the dielectric loss factor of various materials. For example, Vos et al.[14] studied the dielectric loss factors for Al_2O_3 and SiO_2 in the presence of impregnated carbon and reported that the dielectric loss factors increased proportionally to the carbon content. Further, Achour et al.[15] have noticed that carbon black−epoxy resin composites with higher carbon content had higher dielectric loss factor. Moreover, Xu et al.[16] found that the time required to prepare MgS from Mg and S in the presence of graphite in a microwave oven decreased when the amount of graphite was increased.

One of the transition metal oxides showing high catalytic activity toward ORR in AFC is spinel $MnCo_2O_4$. A microwave-assisted method to produce $MnCo_2O_4$ was described in our previous work.[17] It was noticed that spinel $MnCo_2O_4$ formation was not complete when Mn−Co nitrate solutions were heated in a microwave oven (2.45 GHz) at 600 W. Therefore, a microwave energy susceptor was needed, and when carbon was added to the aqueous solution of nitrates, spinel was formed readily at twice-lower power levels. Because the carbon amount can have an effect on the formation of the spinel in microwave oven and on the catalytic properties, it is important to find the optimal amount of carbon. Although the effect of varying carbon amounts on materials' dielectric loss factors is known, to our best knowledge the effect of carbon amount on the microwave-assisted formation and properties of a metal oxide prepared from its nitrates has not been reported. In this work, $MnCo_2O_4$ has been prepared from nitrates mixed with carbon, and the effect of varying carbon amounts on the formation and properties of the spinel catalyst has been studied. The samples were characterized by XRD, TG, TEM, BET surface area, carbon content, and electrochemical measurements.

Experimental Section

Catalyst Preparation. Aqueous solutions of nitrates $Co(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 4H_2O$ in the required stoichiometric proportions were mixed with carbon powder Ketjenblack EC-300N (Akzo Nobel) having a specific surface area of 950 m^2/g. The amount of carbon in the starting mixtures was 7, 13, 18, and 26 wt %. The samples are presented in Table 1. All the mixtures were pretreated by drying at 50 °C in air. The dried mixtures were ground, and after that the nitrates were decomposed in a conventional oven at 200 °C in air. The samples were placed in the oven preheated to 200 °C, and after 15 min the oven was turned off and the samples were allowed to cool to room temperature in the oven. Although the cobalt nitrate decomposes near 300 °C and manganese nitrate decomposes above 200 °C, in the presence of carbon the decomposition of the mixed nitrates was found to be possible near 200 °C. Similarly, Cseri et al.[18] have noticed that metal nitrates supported on clay started to decompose at lower temperatures than the nitrates without a support.

Table 1. Samples Prepared by Microwave-Assisted Route of Synthesis (MARS)

sample	C (wt %) in the nitrate−carbon mixture	C (wt %) after decomposition at 200 °C	type of microwave treatment
7-C	7	9	cyclic
13-C	13	21	cyclic
13-I	13	21	ignition
18-C	18	35	cyclic
18-I	18	35	ignition
26-I	26	39	ignition

After decomposition of the nitrates at 200 °C, the samples were subjected to microwave treatment (2.45 GHz, power 350 W) in the natural air atmosphere prevailing in the oven. Two types of microwave treatments were applied. When using the ignite heating route (I), the samples were heated in a microwave oven until they ignited and began burning with small flames. The initial high oxidation rates of the carbon in the presence of the transition metal ions were then observed. This process was applied on all samples except for 7-C, which did not contain enough carbon to initiate ignition. When using the cycle process (C), the samples were heated in the microwave oven, withdrawn from the oven, cooled to room temperature, and weighed after each heating period. First, the samples were repeatedly subjected to four heating periods of 1 min each in the microwave oven, and an additional heating period of 2 min was then continued until the further heating cycle caused no essential weight change in the mass of the specimen. The cycle process was used for all samples except for 26-I, since its ignition was spontaneous. The masses of the products (oxide on carbon) varied from 13 to 19 g, depending on the residual carbon amount and success of the oxide formation. The decomposition of the nitrates at 200 °C before microwave treatment was necessary for studying the ignition process, because if a sample were subjected to microwave treatment directly after drying at 50 °C, formation of the spinel would require several heating cycles without ignition.

Electrochemical Testing. Gas diffusion electrodes for the oxygen reduction reaction (ORR) were prepared by using the rolling method described by Kiros et al.[19] The catalyst layer contained 60 wt % of the prepared catalyst powder. Electrodes with 4 cm^2 of geometrical areas were tested in an electrolyte concentration of 6 M KOH with the active layer facing the electrolyte, while the rear side of the electrode with the diffusion layer was exposed to the gaseous reactant oxygen. The temperature of the cell was kept at 50 °C and was regulated by a thermostated water bath. The counter electrode was a perforated nickel wire screen. An Hg/HgO reference electrode with the same electrolyte concentration as in the cell was connected to the working electrode by a Luggin capillary, where constant contact made possible the readings of the potentials under intermittent current loads.

Characterization. BET surface areas of the samples were obtained from nitrogen isotherms at liquid nitrogen temper-

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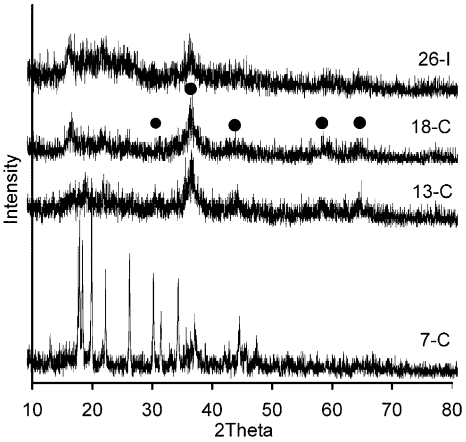

Figure 1. XRD patterns of the samples after decomposition at 200 °C. (●) $MnCo_2O_4$.

ature by an ASAP-2000 Micrometrics, where nitrogen was absorbed after degassing the powders at 100 °C. X-ray diffraction patterns of the samples were obtained by a Philips diffractometer with Cu Kα as a radiation source, using step size 0.02° and step time of 1 s. Surface morphologies and particle size assessments of the different powders were carried out using transmission electron microscopy (TEM) on a JEOL JEM-2000X. Carbon content of the samples was determined by a Leco SC-444 analyzer. Thermogravimetric measurements (TG) were carried out in air atmosphere in a Netzsch STA449C Jupiter analyzer using heating and cooling rates of 5 K/min. For preparing the samples for the TG measurements, aqueous solutions of nitrates $Co(NO_3)_2{\cdot}6H_2O$ and $Mn(NO_3)_2{\cdot}4H_2O$ were mixed with carbon powder already mentioned in the section on catalyst preparation. The amount of carbon in the starting mixtures was the same as that in the MARS samples (Table 1). The mixtures were then dried at 40 °C. The TG measurements are presented here in order to explain the behavior of the MARS samples.

Results and Discussion

XRD Studies. Figure 1 shows the X-ray diffraction patterns of the samples after decomposition of nitrates at 200 °C. The pattern of sample 7-C shows incomplete decomposition of nitrates, while the other samples show spinel $MnCo_2O_4$ formation (JCPDS pattern 23-1237), although the reflections are quite weak.

Figure 2 shows the X-ray diffraction patterns of the samples after microwave treatment. The reflections are stronger than those after the heat treatment at 200 °C, indicating an increase in crystallinity. Moreover, sample 7-C also shows formation of the spinel. However, the formation of spinel in sample 7-C is not complete even after microwave treatment, but the pattern shows along with the spinel structure solid solution of CoO (JCPDS patterns 43-1004 and 9-402) and MnO (JCPDS pattern 7-230). At lower 2θ values, the peaks that do not belong to spinel or the oxides are due to incomplete nitrate decomposition. The pattern of sample 7-C is quite similar to the pattern of sample 18-C after 4 cycles (Figure 3). This implies that the process of spinel formation in the case of 7-C was not complete. Figure 3 also shows that the crystallinity increases during microwave treatment.

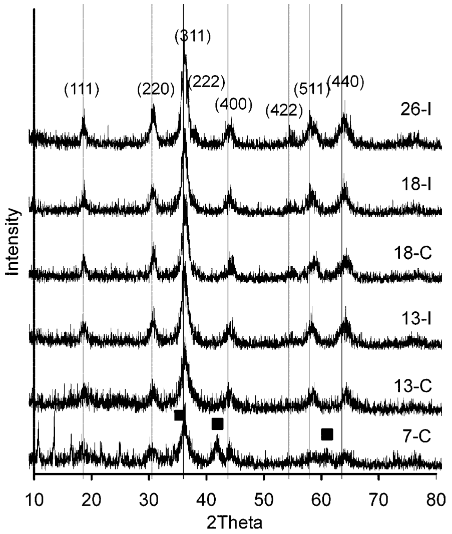

Figure 2. XRD patterns of the samples after microwave treatment. The perpendicular lines show the peak positions of $MnCo_2O_4$ (JCPDS pattern 23-1237). (■) Solid solution of CoO and MnO.

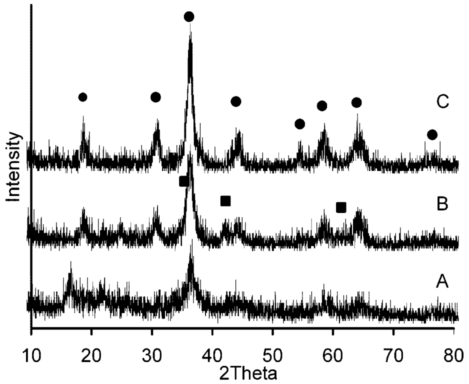

Figure 3. XRD patterns of sample 18-C after decomposition at 200 °C (A), 4 cycles in microwave oven (B), and the cyclic microwave treatment until constant mass was reached (C). (●) $MnCo_2O_4$; (■) solid solution of CoO and MnO.

Figure 2 shows that the peaks have shifted slightly to higher diffraction angles compared to those of spinel $MnCO_2O_4$. The shifting is more pronounced in samples 7-C, 13-C, 13-I, and 18-C, i.e., those with lower carbon content or prepared by the cycle process. Koenig and Brenet[20] reported that oxygen content in $MnCo_2O_x$ was higher in the samples prepared at lower temperatures, resulting in the shift of the peaks to higher 2θ values[20] (JCPDS pattern 32-297). Therefore, it is possible that the shifting shown in Figure 2 is due to slight oxygen excess.

Temperatures. Measurements of the sample temperature with a thermocouple during the microwave treatment failed, and actually, Pert et al.[21] have reported that use of thermocouple during microwave heating could disturb the heating of the sample and give erroneous temperature information. Therefore, for the samples presented in this paper, the temperature measurement during the microwave treatment was not carried out. Temperatures after the microwave treatment were not measured in the case of the cyclic treatment, because immediately after each heating period the sample was covered with a lid. This was done to hinder the access of excess oxygen, which in contact

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Table 2. Mass (% of the Initially Weighed Nitrates and Carbon) for the Different Conditions Prevailing during the Sample Preparation; Temperature in TG Measurement at Corresponding Mass Loss Is Presented in Parentheses

sample	after decomposition at 200 °C	after microwave treatment	theoretical $MnCo_2O_4$ + carbon	theoretical $MnCo_2O_4$
7-C	60 (170 °C)	36 (190 °C)	34	27
13-C	49 (170 °C)	41 (180 °C)	38	25
13-I	49 (170 °C)	31 (330 °C)	38	25
18-C	46 (170 °C)	30 (340 °C)	41	23
18-I	46 (170 °C)	28 (350 °C)	41	23
26-I	59 (150 °C)	24 (370 °C)	47	21

with the hot sample could initiate ignition, as well as to smother the sparkling, which in the case of the samples containing higher carbon amount was observed in the end of the first heating periods. Attempts to measure the temperature for the ignition process after the microwave treatment with a thermocouple failed partly because the sparkling reaction was moving very rapidly from one location to another, and the thermocouple seemed to be too slow to measure the temperatures accurately in this case. However, it was observed that samples 13-I, 18-I, and 26-I ignited after 1.1, 0.9, and 0.2 min, and sparkled or glowed for 4, 10, and 15 min. This shows that the higher the carbon content in the mixture, the sooner the temperature increases during the microwave treatment, and the longer the reaction can proceed after the microwave treatment.

To get more information on the temperatures, the mass losses of the MARS samples were compared with the mass losses of the corresponding TG samples. Table 2 shows the masses of the samples after decomposition and after microwave treatment, as well as the theoretical masses of the spinel with the initial carbon present and the spinel alone. Moreover, the temperatures of the corresponding TG measurements at the same mass loss are shown in parentheses. Table 2 shows that after decomposition treatment, the MARS samples 7-C, 13-C, 13-I, 18-C, and 18-I have the same mass loss as the TG samples have at 170 °C, while the mass loss of 26-I corresponds to a loss at 150 °C. Because the MARS samples weighed much more than the TG samples, and were heated at 200 °C only for 15 min before the oven was turned off, it is possible that the decomposition reaction had not propagated as completely as in the corresponding TG samples at 200 °C. Furthermore, Table 2 shows that after microwave treatment the mass loss of a MARS sample corresponds to an increasing temperature in TG measurement when increasing the amount of carbon from 13 to 26 wt %, and being higher for the ignite-based routes than the cycle-based routes. This observation indicates that the temperature in an ignite process is possibly higher than that in a cycle process. This agrees well with the results presented in Figure 2.

Mass Loss and Formation of Spinel. When the sample mass loss in Table 2 after the decomposition of nitrates is compared with the theoretical amount of spinel with all initial carbon present, it is noticed that all the samples contain some extra mass after decomposition, indicating incomplete nitrate decomposition. Figure 4 shows time–mass curves for the MARS-samples during the cyclic microwave treatment. The starting points of the curves are <60% because most of the nitrates have already decomposed during the heat treatment at 200 °C. Figure 4 shows that the final mass of sample 18-C is smaller than spinel with all initial carbon present but higher than spinel alone. This is the case for samples 13-I, 18-I, and 26-I as well, as can be seen in Table 2, and indicates that some carbon is left in the samples after microwave treatment. Samples 7-C and 13-C, instead, even after microwave treatment show higher mass compared to the mass of spinel with all initial carbon present. Figure 4 and Table 2 show that the mass loss of samples 7-C and 13-C stops when they have reached the same mass as the corresponding TG samples have at 190 and 180 °C. After nitrate decomposition samples 7-C and 13-C contained carbon 9 and 21 wt % (Table 1), and it can be concluded that these amounts of carbon and the type of microwave treatment are not sufficient to raise the temperature of the mixtures to the level where complete nitrate decomposition and/or oxidation of the carbon would occur in the microwave oven.

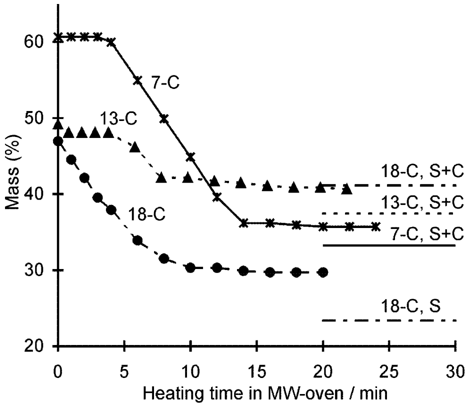

Figure 4. Mass loss during the cyclic microwave treatment. The lines on the right show the theoretical masses of spinel with all initial carbon present (S + C) and spinel alone (S).

According to Figure 4, the mass loss of sample 18-C is noticeable already during the first four 1-min cycles, while the mass of samples 7-C and 13-C remains constant during this period. During the longer cycles (2 min) these samples also start to lose mass, but the mass change of sample 7-C takes longer than that for the other samples. This is because 7-C still has a considerable amount of nitrates left after decomposition as can be seen in Figure 1. According to Figure 4, the decomposition of nitrates in sample 7-C proceeds at a quite constant rate for several minutes even though this sample does not contain much carbon. After this constant period the mass loss ceases, but the spinel formation was not complete as described above and as can also be seen in Figure 2. It can be concluded that the nitrate–carbon mixture absorbs microwaves better than the forming oxide–carbon mixture, and the reaction can proceed as long as there are enough nitrates left in sample 7-C. When most of the nitrates have decomposed, the formed oxides do not absorb microwaves well enough, and the amount of carbon is too little to raise the temperature high enough to produce pure $MnCo_2O_4$.

Carbon Content, Specific Surface Area, and Particle Size. It can be concluded from the XRD and

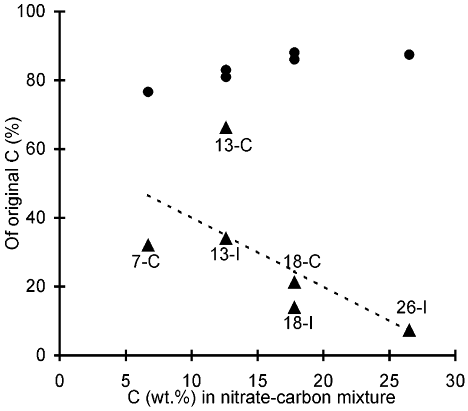

Figure 5. Remaining carbon as % of original carbon amount after decomposition at 200 °C (●) and after microwave treatment (▲).

mass loss measurements that the less is the carbon content in the initial mixture, the lower is the tendency of the metal ions and carbon to proceed with the oxidation reaction. Thus, there exists a minimum level of carbon composition to be able to create a surface contact with the metal ions with consequent burnout. Sample 7-C contained 9 wt % of carbon after heat treatment at 200 °C, and this amount was not enough for complete spinel formation during microwave treatment. Carbon content of 21 wt % in sample 13-I was enough for further spinel formation in the ignite process. Even though the X-ray pattern of sample 13-C, which was prepared by the cyclic route, shows formation of spinel, according to mass loss calculations it can be suspected that some of the nitrates are not fully decomposed. Samples 18-C and 18-I contained 35 wt % of carbon after decomposition of the nitrates, and this amount was enough for further spinel formation in both the studied cases. Increasing the content of carbon beyond this amount to 39 wt % in sample 26-I did not yield any benefit, although the formations of spinel were still abundant.

Figure 5 shows carbon loss during decomposition of nitrates and microwave treatment. During the decomposition the carbon loss was between 10 and 23% of the original carbon content. Although the TG measurements showed that the carbon started to burn not before 550 °C in air, it is possible that the carbon starts to be oxidized at much lower temperatures when in contact with a catalyst, e.g., a metal ion. The catalytic effect of a metal is reported, for example, by Bekyarova et al.[22] for Co-impregnated carbon. Furthermore, Vos et al.[14] reported that when Al_2O_3 and SiO_2 impregnated with carbon were heated in a microwave oven in He gas containing only 0.5 vol % O_2, carbon dioxide formation was at a maximum between 300 and 500 °C, but had started already below 200 °C. In the present study the oxidation of carbon even at lower temperature can be explained by the effect of forming oxidative nitrogen oxides. During the microwave treatment, 20−90% of the remaining carbon was oxidized, which corresponds to 34−93% of the original carbon amount. The higher was the carbon content in the initial nitrate−carbon mixture, and therefore also before microwave treatment (see Table 1), the higher became the amount of oxidized carbon during the microwave treatment. Further, more carbon was oxidized during the ignite treatment than during the cycle treatment.

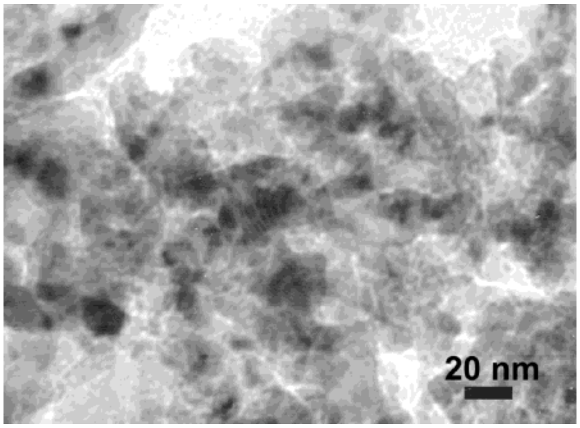

Figure 6. TEM photograph of spinel prepared by MARS (sample 18-I).

Table 3. Carbon Content and Specific Surface Area of the Catalysts Prepared by MARS, and Voltage in Electrochemical Measurements of the Electrodes Containing the MARS Samples as Catalysts

sample	C (wt %)	BET surface area (m^2/g)	mV at 100mA/cm^2
7-C	6	11	−254
13-C	21	101	−137
13-I	14	110	−152
18-C	13	111	−144
18-I	9	96	−133
26-I	8	83	−218

Increasing the content from 18 to 26 wt % in sample 26-I did not improve the outcome of the final product. Instead, the increase resulted in lower carbon content of the final catalyst consequently leading to lower specific surface area as shown in Table 3. This could be explained by the possible high-temperature propagation and burnoff of the excess carbon during the interaction process between carbon, metal ions, and nitrates. Moreover, Table 3 shows that the BET surface areas of the powders prepared by the microwave technique increase with increasing carbon content of the spinel−carbon mixture. Carbon contents of the samples prepared by the cycle route are somewhat higher than those of the samples prepared by the ignite route.

Figure 6 shows a TEM micrograph of sample 18-I, presenting a typical powder prepared by a successful microwave-assisted synthesis, showing particle sizes mostly around a few nm and some agglomerates smaller than 30 nm. Moreover, the figure shows that the spinel particles (dark areas) are well distributed and dispersed throughout the remaining carbon (lighter areas).

Electrocatalytic Performance. Figure 7 shows the electrocatalytic activity of the electrodes toward oxygen reduction reaction, measured after 1 day of activation of the electrode. The smaller is the voltage drop at a certain current density, the better is the catalytic activity for ORR. Figure 7 shows that the catalytic activity of the samples increases in the following order: 7-C < carbon < 26-I < 13-I < 13-C ≈ 18-C ≈ 18-I. In other words, sample 26-I, having lower specific surface area, did not show better catalytic activity than the carbon alone. Furthermore, sample 7-C, which did not

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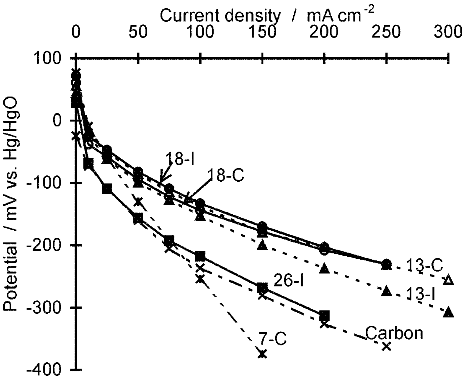

Figure 7. Polarization curves of the electrodes containing MARS catalysts.

have complete spinel formation, showed even lower catalytic activity than the carbon alone. The other samples showed relatively high or high catalytic activity for ORR. In the literature we did not find current−voltage data for $MnCo_2O_4$ measured for ORR at higher current densities (>50 mA/cm^2) and in conditions substantially similar to those in this report. In our previous report,[17] CoTPP was used together with the spinel as catalyst, and therefore the values are not comparable to the current values. Figure 7 shows that, for example, sample 18-C shows voltage drops of 50 and 60 mV when increasing the current density from 50 to 100 mA/cm^2 and from 100 to 200 mA/cm^2, respectively. Some other Co-rich spinels, for example Co_3O_4,[23,24] $NiCo_2O_4$,[25−27] and $LiMn_{0.4}Co_{1.6}O_4$,[28] measured in 5−7 M KOH and at 20−60 °C have shown corresponding voltage drops of 20−50 mV and 20−90 mV. However, in addition to the electrolyte concentration and temperature, also composition and pressure of the reactant gas, catalyst loading, electrode thickness, IR-correction, and the manufacturing method of the electrode have effects on the current−voltage curves, although these parameters are not always mentioned.

The decay rates at 100 mA/cm^2 for the MARS samples 18-C and 18-I were found to be low (0.08−0.09 mV/h), as presented in Figure 8. The sharp voltage change during the first day is due to wetting, activation, and stabilization of the electrode. The other samples were not very stable at 100 mA/cm^2 for longer periods of time.

As Table 3 shows, the current densities at the constant potential of 100 mA/cm^2 of the gas-diffusion electrodes of the spinel−carbon mixtures increased with increasing specific surface areas. But, increasing the BET surface areas beyond 90 m^2/g did not result in better performance. Similar results have been reported earlier: for cathode reactions, the correlation of BET surface areas to activity have shown that increasing the BET surface areas beyond 80 m^2/g did not yield any significant gain in the performance of the electrodes.[19]

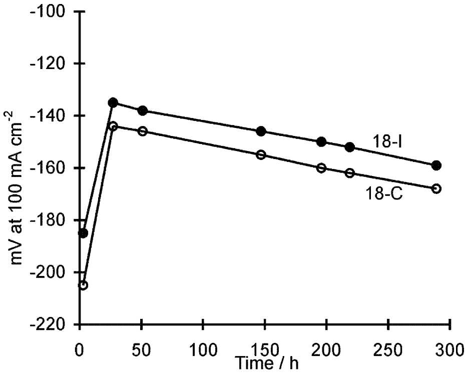

Figure 8. Stability of the electrodes at 100 mA/cm^2.

Conclusions

Mixtures of Mn- and Co-nitrate and carbon containing varying amounts of carbon (7, 13, 18, and 26 wt %) were heat-treated at 200 °C, and the decomposition degree of nitrates depended on the amount of carbon. When the carbon amount was 7 wt %, nitrate decomposition was clearly incomplete. When the nitrate−carbon mixture contained 13 wt % or more carbon, the formation of spinel $MnCo_2O_4$ could be noticed. However, according to mass loss calculations, even the mixtures with higher carbon content contained some residual nitrates after decomposition at 200 °C. The final decomposition of nitrates and increase in $MnCo_2O_4$ crystallinity occurred during further heat treatment at 350 W in a 2.45-GHz microwave oven. After decomposition of nitrates at 200 °C, the mixtures contained 9, 21, 35, and 39 wt % of carbon, and the minimum of 21 wt % of carbon as a microwave susceptor was needed for complete spinel formation.

Most of the carbon was oxidized during the microwave treatment. When increasing the carbon content above 7 wt %, it was noticed that the higher the initial carbon content in the nitrate−carbon mixture was, the lower the carbon content was after the microwave treatment. This is because when the amount of carbon in the mixtures increased, the temperature during the microwave treatment possibly increased, resulting in the oxidation of more carbon. When the carbon content of the final catalyst decreased, the specific surface area also decreased. Compared to the ignite process, the cycle process resulted in slightly higher carbon content in the final catalyst. When considering the catalytic activity toward oxygen reduction reaction in alkaline electrolyte, the carbon amount of 18 wt % in the initial nitrate−carbon mixture was most preferable.

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