

# Microwave synthesis of catalyst spinel $\text{MnCo}_2\text{O}_4$ for alkaline fuel cell

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## Abstract

Spinel,  $\text{AB}_2\text{O}_4$ , are promising catalysts for the oxygen reduction reaction in alkaline fuel cells since they have no noble metals and can be prepared by rather simple methods. In this work the spinel  $\text{MnCo}_2\text{O}_4$  was fabricated from decomposition of salts and subsequent heat treatment in microwave and conventional ovens. The catalytic activity of spinels for the oxygen reduction reaction was examined in alkaline conditions in a specially designed test bed. XRD, SEM, surface area, and carbon content measurements were used to analyze the prepared powders. Spinel was not detected for treatment in a microwave oven at 650 W power without carbon, but in the presence of carbon it was formed at 125 W rapidly (in a few minutes). These spinels have smaller particles and higher specific surface area and they have demonstrated higher catalytic activity for the oxygen reduction reaction than the spinels prepared in a conventional oven. The Microwave technique proved to be a favorable and fast way to prepare catalytically active spinel  $\text{MnCo}_2\text{O}_4$  for alkaline fuel cells. Tested fuel cells are being adapted for transport applications in vehicles. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Spinel;  $\text{MnCo}_2\text{O}_4$ ; Alkaline fuel cell; Microwave; Catalyst

## 1. Introduction

Alkaline fuel cells (AFC) consist of hydrogen and air electrodes, with an alkaline electrolyte between them. In the case studied hydrogen is usually stored in metal hydride form. Oxygen taken from surrounding air diffuses through the porous air electrode and is being reduced in the active layer of an air electrode acting as cathode. Electrochemical evaluation of a sintered metal hydride electrode for electric vehicle application has been reported earlier [1]. Preparation of air electrodes [2,3] and the optimal structure of porous air electrodes [4] have also been previously reported. The aim of this work is to fabricate a cheap catalyst with high catalytic activity for oxygen reduction. Spinel  $\text{AB}_2\text{O}_4$  are promising catalysts for this purpose since they have no noble metals and can be prepared by rather simple methods. Mixed valence spinel oxides may exhibit electrical conductivity or semi-conductivity enabling their direct use as electrode materials [5]. The cations can change their oxidation state, and “electroconductivity chains” are thus formed providing movement of either electrons or holes [6]. Spinel  $\text{MnCo}_2\text{O}_4$  has shown good catalytic activity for the oxygen reduction reaction (1) in alkaline conditions [5]:



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The catalytic activity of spinels depends greatly on the preparation method and conditions [7,8]: annealing time, temperature, nature and pressure of surrounding atmosphere, etc. Methods to synthesize spinel oxides applying conventional heating are, e.g. decomposition of salts followed by heat treatment [9], spray pyrolysis technique [8], sol-gel [10], and combustion process [11,12]. Li et al. [13] have prepared nanoscale spinel-type oxides, and they noticed that the addition of carbon black into solutions of nitrates and citric acid has weakened the agglomerates of the oxide particles and increased the surface area.

The Microwave assisted route is a novel method of synthesis and is a very rapidly developing area of research [14]. In a microwave oven, heat is generated internally within the sample itself by interaction of microwaves with the material [15] instead of originating from an external heating source as in conventional oven. Microwave synthesis is generally considered fast and very energy efficient. Temperature measurement in a microwave oven is not straightforward, but it has been reported that reactions occur at lower temperatures in a much shorter time in microwave synthesis than in conventional methods [16]. Microwave synthesis has given products with good phase purity and degree of crystallinity [17,18] and nanoscale particles [19,20]. Also larger surface area [21] and smaller particles [22], but also bigger crystallites [23] compared to conventional methods have been obtained. Recently several spinels [24–26] and other oxides have been synthesized by applying

microwave irradiation. The effect of microwaves varies greatly from material to material. If the starting materials are not very good susceptors to microwaves, it is necessary to use a secondary susceptor that assists the initial heating. Amorphous carbon powder, e.g. can be used for this purpose since it absorbs microwaves very rapidly [14]. In this study, we have used a microwave technique, where carbon powder with high surface area, mixed with aqueous solutions of salts, acts both as a microwave energy susceptor and surface-increasing agent to produce nanoscale  $\text{MnCo}_2\text{O}_4$  powder.

## 2. Experimental

### 2.1. Preparation in microwave oven

Carbon powder was mixed with aqueous solutions of nitrates or acetates. Two types of carbon were used: Ketjenblack<sup>®</sup> EC-300N and Ketjenblack<sup>®</sup> EC-600JD (Akzo Nobel). Typical surface areas for these carbons are 950 (EC-300N) and 1250  $\text{m}^2/\text{g}$  (EC-600JD). In most cases the mixtures were heated immediately after preparation, but some samples were let to stand in air for 2 days before heating. The mixtures (3–270 g) were heated in microwave oven (2.45 GHz) using power levels from 125 to 650 W for few minutes. Total heating time has been considered as the total time of microwave irradiation being supplied to the specimen. For set power level of, e.g. 500 W of the 650 W oven, the residence time of the mixture in the oven is  $650/500 = 1.3$  times longer, than actual heating time. Two atmospheres were used during heating: air and nitrogen with 0.5%  $\text{O}_2$ . After each heating period the mixture or powder was cooled, weighed, and ground. Heating was continued until further heating cycle caused no essential change in mass of the specimen.

### 2.2. Preparation in conventional oven

Co and Mn nitrates were dissolved in small amount of water, which was vaporized by heating and stirring. Nitrates

were decomposed at 250 °C for 2 h and calcinated in air at 900 °C for 8 h. Spinel was also prepared at 250–500 °C in air for 8–48 h, with carbon mixed in the starting solutions. However, some of the these powders contained not only cubic spinel  $\text{MnCo}_2\text{O}_4$  but also tetragonal mixed spinel  $(\text{Co}, \text{Mn})(\text{Co}, \text{Mn})_2\text{O}_4$ . Moreover, the powders prepared at 250–500 °C showed no noticeable catalytic activity.

### 2.3. Characterization

Powder X-ray diffraction patterns were obtained using Philips diffractometer and  $\text{Cu K}\alpha$  radiation. To investigate the characteristics of powders, scanning electron microscopy (SEM) micrographs were taken with JEOL JSM-840 with an EDS germanium detector. Carbon content of the powders was measured by Leco SC-444 analyzer. The specific surface areas of the powders were measured by the Brunauer–Emmet–Teller (BET) method ( $\text{N}_2$  adsorption).

## 3. Testing the catalytic activity

The catalytic activity of the prepared spinels for oxygen reduction reaction (1) was measured in an open half-cell and in a fuel cell test bed. For testing the catalytic activity in a half-cell, flat electrodes of 10  $\text{cm}^2$  of active area were prepared. The gas-diffusion layer consisted of 60 wt.% PTFE (polytetrafluoroethylene, Dyneon TF 5032) in acetylene black (SKW Piesteritz P 1042 S-uv) and a nickel mesh as current collector. The active layer contained the same diffusion material with 14  $\text{mg}/\text{cm}^2$  of a prepared powder. The electrodes were pressed and heat-treated at 340 °C. The polarization curves, referred to a  $\text{Hg}/\text{HgO}$  electrode, were measured in 6 M KOH at 60 °C in air.

Fuel cell performance was examined with 200  $\text{cm}^2$  cylindrical cells in a specially designed test system (Fig. 1). One cell consists of two tubes, one within the other. Structure of cylindrical air electrode (outer tube) with spinel powder as catalyst is similar with flat ones. Air

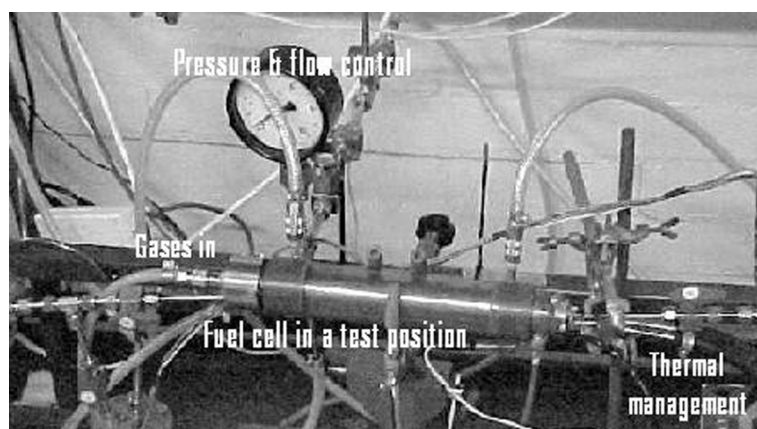


Fig. 1. Fuel cell test system.

electrode is under normal air pressure during measurement. Air flow used in tests is 700 l/h. Catalyst used in active layer of hydrogen electrode is Pt/Pd-mixture in charcoal (Johnson Matthey). Hydrogen pressure at inner electrode is 0.4 MPa (abs) during measurement. Between these two cylinders alkaline electrolyte is placed. Measurements have been carried out at 70 °C.

## 4. Results and discussion

### 4.1. Difference between microwave and conventional heating

Formation of spinel  $\text{MnCo}_2\text{O}_4$  was confirmed by X-ray diffraction for both materials prepared in conventional and in microwave oven (Fig. 2). Peak broadening of the samples prepared by microwave technique might be due to nanoscale particles as well as to variation of oxygen content or non-uniform strain [27] in the spinel crystallites. Smaller peak intensity of the samples prepared in microwave oven may be referred to lower crystallization degree or to lower portion of spinel (78 wt.%) in the powder.

SEM micrographs show (Fig. 3) that the spinel prepared in an ordinary oven at 900 °C consists of larger (sintered or agglomerated) particles (about 0.2–3  $\mu\text{m}$ , Fig. 3a) than that prepared in the microwave oven. Microwave technique produces nanoscale powders, where smaller particles possibly form only weak agglomerates (Fig. 3b). The specific surface area of the powders prepared at 900 °C is quite small (0.7  $\text{m}^2/\text{g}$ ). The powders prepared by microwave technique have larger surface areas: the powder containing only 4 wt.%

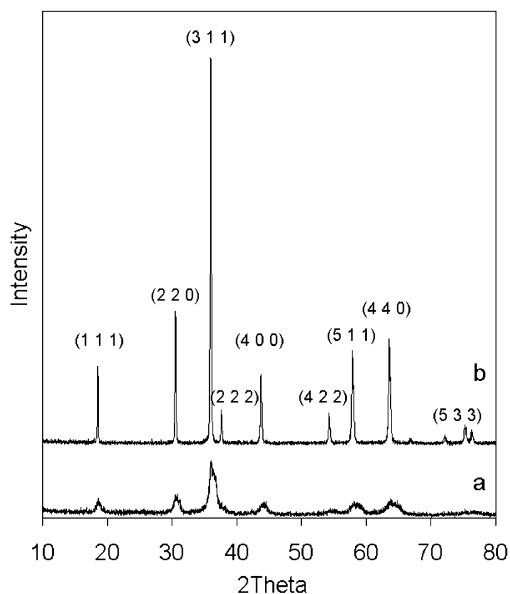


Fig. 2. XRD-patterns of  $\text{MnCo}_2\text{O}_4$  prepared from nitrates (a) mixed with carbon EC-300N by microwave technique at 400–550 W in air (the powder contains 22 wt.% of carbon), and (b) in conventional oven at 900 °C for 8 h in air.

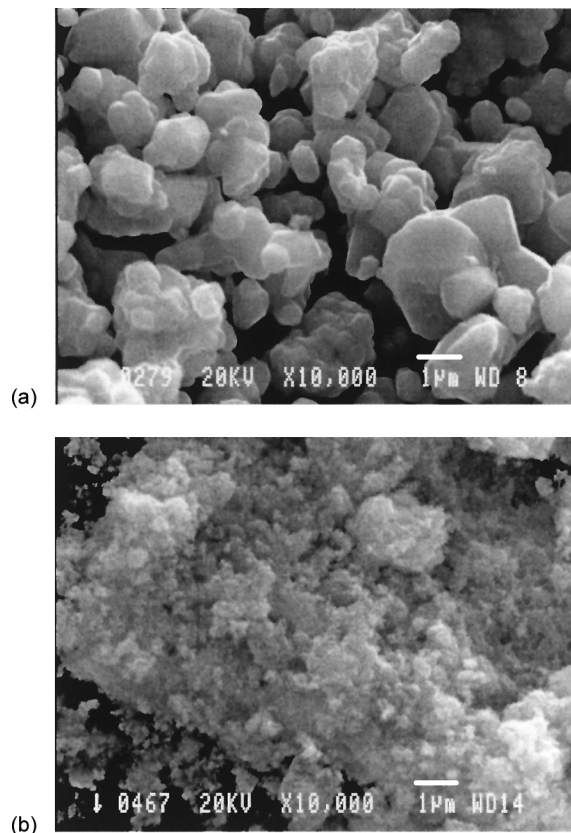


Fig. 3. SEM micrographs of  $\text{MnCo}_2\text{O}_4$  prepared from nitrates (a) in conventional oven at 900 °C, (b) mixed with carbon EC-300N by microwave technique at 400–550 W in air (the powder contains 22 wt.% of carbon).

of carbon has surface area of 40  $\text{m}^2/\text{g}$ , and it increases with increasing carbon content (Fig. 4) as can be expected.

### 4.2. Heating time

For the microwave technique described, heating time increases with increasing the mass of specimen. This dependence, however, is not linear. To prepare 1.5 g of spinel in carbon total heating in microwave oven of 11 min was necessary, but to prepare 14 g only 26 min. It must be noticed that the starting mixtures for larger samples contained naturally more water than the starting mixtures for small samples, and considerable part of the energy was used to heat and vaporize this water. A small sample dried at room temperature and then heat-treated in microwave oven was used to test a possibility to prepare spinel from dried mixture. There is no significant difference in XRD-patterns of the samples prepared from wet and dry starting mixture (Fig. 5), and their specific surface areas are quite close to each other: 165 and 150  $\text{m}^2/\text{g}$  for the powders from wet and dry method, respectively. As the needed heating time in both cases was quite similar, drying does not seem to reduce the total heating time, at least when small amounts are prepared (about 1 g).

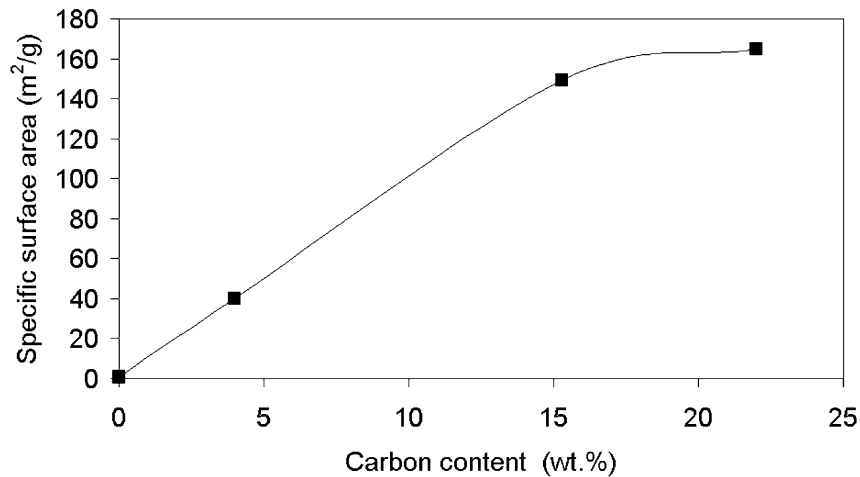


Fig. 4. Specific surface area of the  $\text{MnCo}_2\text{O}_4$  powders as a function of carbon content.

#### 4.3. Effect of carbon and heating conditions

When samples were prepared directly from salt solutions without addition of carbon at power of 650 W in air, spinel  $\text{MnCo}_2\text{O}_4$  was not detected. In the case of acetates as starting materials, no formation of any oxide phase was noticed (Fig. 6a). In the case of nitrates, peaks of spinel have moved somewhat towards larger angles, indicating formation of spinel  $\text{MnCo}_2\text{O}_{4+x}$ , but with other undesirable peaks (Fig. 6b). When carbon was added to the aqueous solution of acetates, spinel was formed already at 125 W in air (Fig. 6c). This can be explained by carbon acting as an internal susceptor that absorbs microwaves better than the used salts [14]. The amount of carbon oxidized during the preparation, i.e. burned out and used for metal oxides reduction, depends on the power and the heating time.

Too high power levels or too long heating periods caused burning of carbon and undesirable reduction of materials into Co, CoO and MnO (Fig. 7c and d). In air atmosphere, medium power levels (400–550 W) and a heating period of 1–3 min were suitable. In most cases acetate–carbon mixtures reacted more vigorously and started to burn at lower power levels than nitrate–carbon mixtures. When the nitrogen (0.5%  $\text{O}_2$ ) was used, the reaction was less vigorous, but the lack of oxygen caused reduction of metals in the most cases (Fig. 7b).

Type of carbon was found to have effect on preparation of the powder. The carbon with higher surface area (EC-600JD) as addition material, compared to the carbon with lower surface area (EC-300N), caused broader peaks (Fig. 8), bigger specific surface area (40  $\text{m}^2/\text{g}$  compared to 14  $\text{m}^2/\text{g}$ ), and better catalytic activity of the final powder. However, the

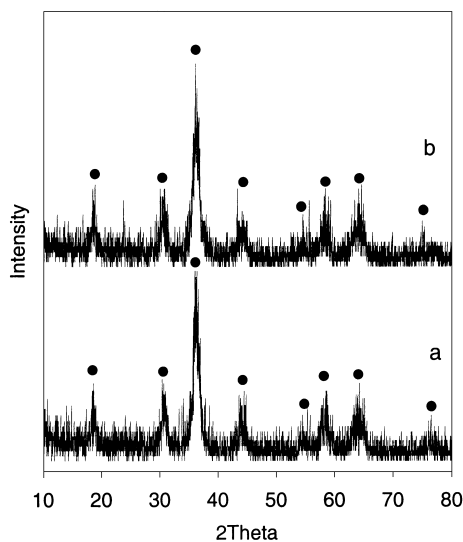


Fig. 5. XRD-patterns of powders prepared by microwave technique from mixture of nitrates and carbon EC-300N (a) wet; (b) dried. (●)  $\text{MnCo}_2\text{O}_4$ .

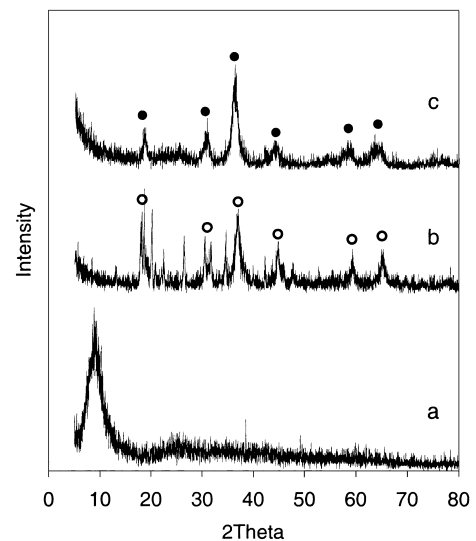


Fig. 6. XRD-patterns of powders prepared at 650 W without carbon (a) from acetates, (b) from nitrates, and (c) from acetates mixed with carbon EC-300N at 125 W. (●)  $\text{MnCo}_2\text{O}_4$ ; (○)  $\text{MnCo}_2\text{O}_{4+x}$ .

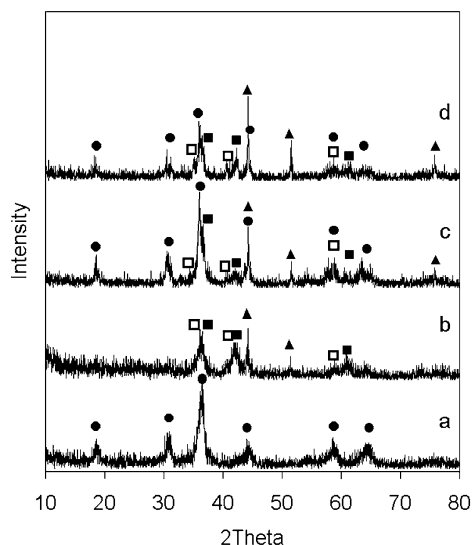


Fig. 7. XRD-patterns of powders prepared from acetates mixed with carbon EC-300N by microwave technique. (a) No flames during preparation in air, (b) in low oxygen atmosphere, (c) short burning time, (d) long burning time during preparation in air. (●)  $\text{MnCo}_2\text{O}_4$ ; (▲) Co (■) CoO; (□) MnO.

mixture prepared from EC-600JD and nitrates burned more easily than the EC-300N-nitrate mixture. When the two samples had been heated for some time and when the mass was still changing, samples were taken to see if the spinel had formed already. It can be seen that in the case of EC-300N formation of spinel has not started (Fig. 8a), but in the case of EC-600JD formation of spinel has well proceeded, even though some peaks of Mn–Co oxide can be seen (Fig. 8c). Heating was continued till mass change became

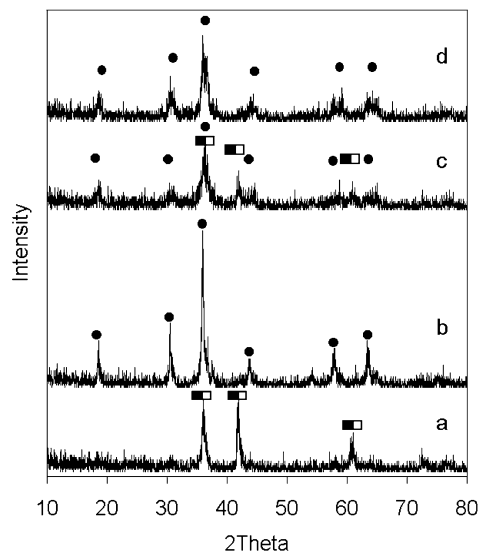


Fig. 8. XRD-patterns of powders prepared at 400 W from nitrates and carbon type (a) EC-300N, (b) EC-300N, additional heating of 13 min, (c) EC-600JD, (d) EC-600JD, additional heating of 4 min.

negligible, and it required additional heating of 13 min in the case of EC-300N and 4 min in the case of EC-600JD. At this stage spinel has formed in both cases (Fig. 8b and d).

#### 4.4. Fuel cell performance

The measurements shown here have been performed with short activation time (1–3 h with  $100 \text{ mA/cm}^2$ ), and it must be noticed that the performance is improved with longer

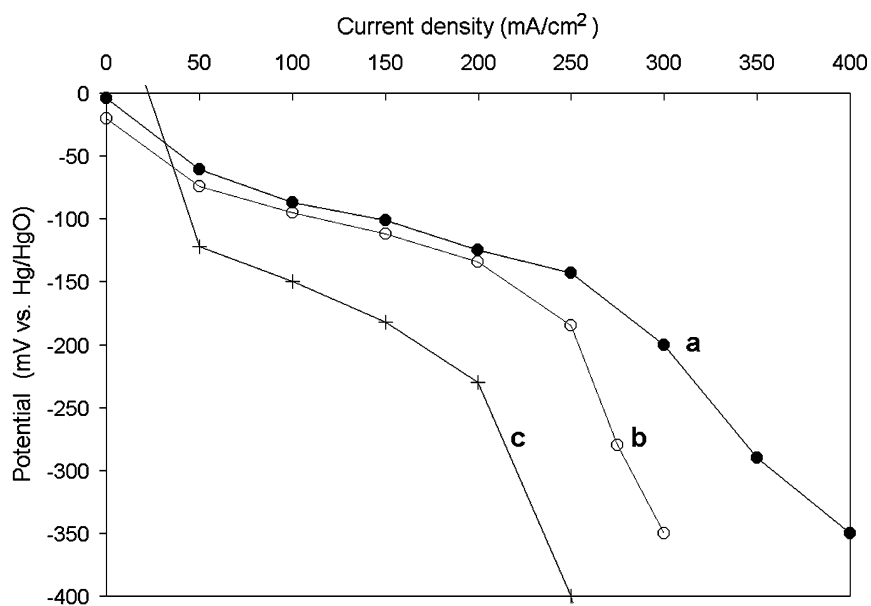


Fig. 9. Polarization curves of air electrodes containing spinel as catalyst, measured in 6 M KOH in air. Catalysts prepared from nitrates and carbon EC-300N by microwave technique (a) in air, (b) in low oxygen atmosphere, (c) from nitrates in conventional oven at  $900^\circ\text{C}$ .

Table 1

Samples prepared by microwave technique (aqueous solution of salts mixed with carbon EC-300N) in air and in nitrogen (0.5% O<sub>2</sub>)

Catalyst	Starting salt	Stayed in air before heating (days)	Atmosphere	C	Phases
NS <sub>air</sub>	Nitrates	2	Air	22	Cubic spinel MnCo <sub>2</sub> O <sub>4</sub>
NS <sub>low</sub>	Nitrates	2	N <sub>2</sub>	30	–
A <sub>air</sub>	Acetates	–	Air	28	Cubic spinel MnCo <sub>2</sub> O <sub>4</sub>
A <sub>low</sub>	Acetates	–	N <sub>2</sub>	57	Cubic Co, CoO, MnO
N <sub>air</sub>	Nitrates	–	Air	29	Cubic spinel MnCo <sub>2</sub> O <sub>4</sub>
N <sub>low</sub>	Nitrates	–	N <sub>2</sub>	55	Cubic spinel MnCo <sub>2</sub> O <sub>4</sub>

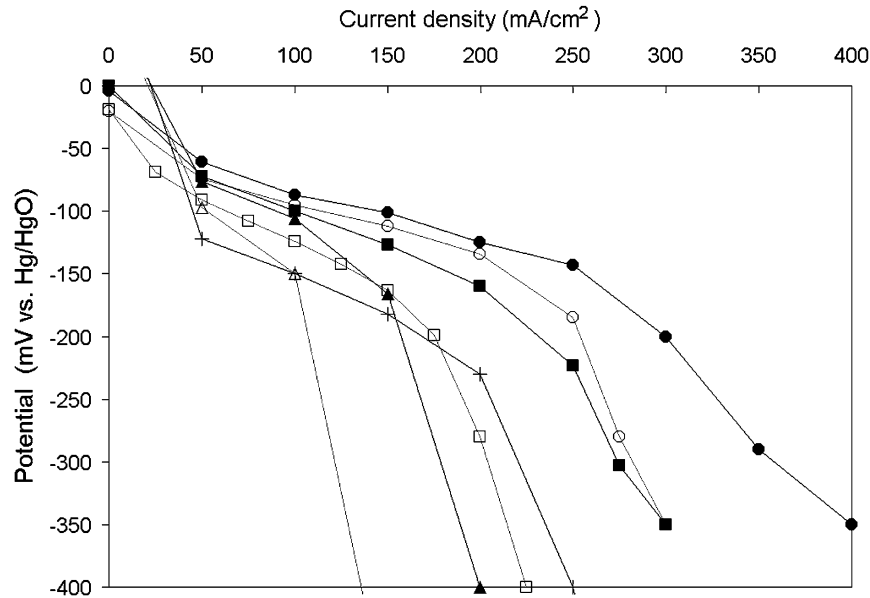


Fig. 10. Polarization curves of air electrodes containing catalysts prepared by microwave technique, measured in 6 M KOH in air. Samples as named in Table 1. (●) NS<sub>air</sub>; (○) NS<sub>low</sub>; (■) A<sub>air</sub>; (□) A<sub>low</sub>; (▲) N<sub>air</sub>; (△) N<sub>low</sub>; (+) Spinel prepared in conventional oven at 900 °C.

activation. During the measurements air is allowed to diffuse freely into the cell, without pumping. The situation in a real alkaline fuel cell is better; air is pumped in with a certain flow. Spinel prepared by microwave technique have demonstrated higher catalytic activity for the oxygen reduction reaction (1) than the spinels prepared in an ordinary oven (Fig. 9). The best results were observed, when the mixture was allowed to stand at room temperature for 2 days before microwave treatment. During this time the salt solution has infiltrated into carbon pores, and the mixture has been homogenized. Table 1 shows the samples prepared by microwave technique in air and in a low oxygen atmosphere. Preparation in air has given in most cases better results than preparation in a low oxygen atmosphere (Fig. 10). Catalytic activity of spinels prepared in a microwave oven was better also for fuel cell measurements.

## 5. Conclusions

The microwave technique used proved a favorable and fast way to prepare catalytically active spinel MnCo<sub>2</sub>O<sub>4</sub>.

Spinel prepared by the microwave technique showed significantly higher catalytic activity than spinel prepared in a conventional oven at 900 °C. Conventional preparation gives microscale (0.2–3 μm) powders, but the microwave technique resulted in nanoscale powders. Spinel was not formed without carbon addition even at 650 W, but when carbon was mixed into the starting solutions, spinel was formed at 125 W. High power levels and long heating periods caused undesirable burning of carbon and reduction of metals, but moderate power levels and short heating periods gave good results. Heating in an air atmosphere in a microwave oven resulted in powders with more pure spinel phase than heating in a low oxygen atmosphere. When the starting mixture was allowed to stay in air for 2 days before heating, the catalytic activity was better compared to samples heated directly after mixture preparation. The microwave technique seems a very promising method for synthesizing catalyst. Experiments have shown that it is possible to fabricate catalytically active material. The advantages of microwave-manufactured spinels were successfully demonstrated in electrochemical measurements and real fuel cell tests.

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