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Improved Pt alloy catalysts for fuel cells

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Abstract

Supported Pt–Co–Cr alloy catalysts on graphitized carbon black showing increased activity and stability as electrode catalysts for oxygen–reduction reaction in phosphoric acid fuel cells have been developed by co-precipitation of the corresponding metal nitrates. XRD investigations showed that a tetragonal ordered structure was formed upon thermal treatment. The formation of this structure required temperatures above 873 K. Although two-step and other sequential methods are known for the preparation of such catalysts, the newly developed method described here will led more efficiently to catalysts, having a small particle size, of the platinum cobalt chromium alloy.

Keywords: Platinum alloy catalysts; Fuel cells

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1. Introduction

Fuel cells can provide a clean and efficient conversion of fuels directly to electricity. The efficiency of common energy generation devices like heat engines, which rely on the combustion of fossil fuels, are limited by the Carnot cycle. The maximum efficiency of such practical heat engines is usually ≤40%. In contrast to that fuel cells are capable of 40%–60% fuel-to-electricity efficiency by electrochemical conversion of fuels. If the waste heat can be used, even higher efficiencies of about 80% are possible [1].

Among the various fuel cell types, the phosphoric acid fuel cell is believed to be the fuel cell technology that is closest to commercialization. However, the market entry of this technology is retarded by high initial costs. Recent estimations of the installed stationary power fuel cell plants assumed that the world-wide demand will be about 90 MW by 1998 and 190 MW by 2000, respectively [2]. To achieve these targets, the costs per kW have to be cut by half. Factors such as cell performance and life time are determining the overall output of the fuel cell power plant. Therefore, increased catalyst activity and particularly catalyst stability would be beneficial from an economic point of view.

Different approaches were made to increase catalyst activity and stability in the past. It is believed that the apparent mode of catalytic enhancement with alloyed platinum catalysts for oxygen reduction based on the leaching of the non-noble metal components from the alloy crystallite surfaces. So far, Pt–Co–Cr alloy combinations are one of the most favoured combinations for the oxygen–reduction reaction (ORR) [3–5]. Because of this reason, the influence of different preparation methods on the electrochemical performance of alloyed Pt–Co–Cr/C

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electrode catalysts was investigated in the present paper.

2. Experimental

10 wt.-% Pt catalysts composed of about 50 atom-% Platinum, 30 atom-% Cobalt and 20 atom-% Chromium were prepared on a graphitized carbon black (BET surface area: 85 m^2/g) by co-precipitation and according to the state-of-the-art methods. The latter included two-step processes [6,7] as well as stepwise addition of active components [8]. As metal precursors, preferably, chlorides and/or nitrates were used. After deposition of the active components, alloying was achieved for all samples equally by thermal treatment under nitrogen atmosphere for 1 h at 1173 K.

Structural information about the catalysts were received from X-ray diffraction (XRD) analysis. The experiments including the temperature-dependent analysis were performed in the transmission mode with an X-ray powder diffraction apparatus STOE STADI/2P using Cu Kα radiation with a wavelength of 1.540598 Å. The average particle size of the Pt alloy crystallites was determined according to the Scherrer equation by peak broadening of the diffraction line of the (101) lattice plane for tetragonal structure. Furthermore, the lattice contraction of the alloyed metal crystallites was calculated for platinum from the shifted peak position compared to the face-centred cubic phase of pure platinum.

Porous gas diffusion electrodes having a Pt loading of 0.5 mg Pt/cm^2 and a polytetrafluoroethylene content of 30 wt.-% were prepared on a hydrophobic graphite paper for the electrochemical tests. The oxygen reduction was carried out in a half-cell equipment at 463 K and atmospheric pressure in 103 wt.-% phosphoric acid using O_2 as reactant. The reference electrode was a dynamic hydrogen electrode. After 3 h and 22 h, respectively, the cell performance was recorded in order to assess about catalyst activity and stability.

3. Results and discussion

Some characteristic XRD data depending on the preparation method are given in Table 1. The catalysts 3, 4 and 7 have the smallest particle size of the series; consequently, the peaks of the XRD diagram are broader than the ones of other samples containing larger metal crystallites. Obviously, these one-step preparations are preferably suitable for the generation of small alloyed particles on the carbon black support.

Although the catalysts contain cobalt and chromium apart from platinum, no significant metal phases of these single elements can be observed by XRD analysis. The XRD diagram of catalyst 4 depicted in Fig. 1 may serve as a typical example for the whole catalyst series. Fig. 1a shows the XRD diagram of a catalyst after prolonged thermal treatment (> 1 h) at 1173 K resulting in an alloy particle size of about 12 nm. Fig. 1b displays the catalyst treated according to the standard pro-

Table 1
XRD data of Pt–Co–Cr alloy catalysts depending on the preparation method depositing Pt first or simultaneously with the other metal compoments

Catalyst	Preparation method	Precursor			Average particle size (nm)	Structure/lattice constant (Å)
		Pt	Co	Cr		
1	2-step	chloride	nitrate	chromate	7.2	weak/3.852
2	2-step	chloride	nitrate	nitrate	10.1	strong/3.782
3	1-step (stepwise)	chloride	chloride	chloride	5.6	strong/3.784
4	1-step (co-precip.)	nitrate	nitrate	nitrate	5.7	medium/3.802
5	2-step	nitrate	nitrate	chromate	7.7	weak/3.842
6	2-step	nitrate	nitrate	nitrate	16.5	strong/3.802
7	1-step (stepwise)	nitrate	chloride	chloride	6.1	strong/3.797

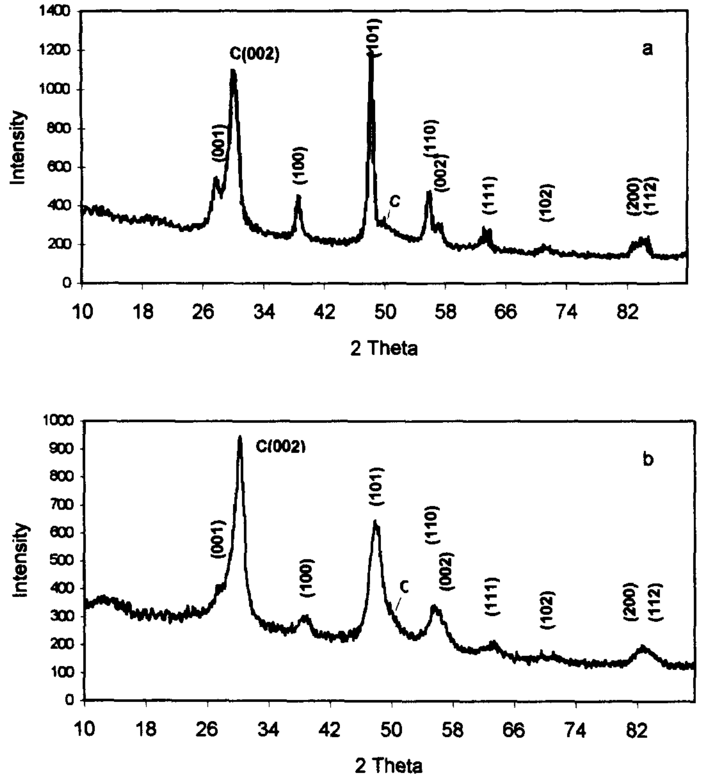

Fig. 1. XRD of catalyst (4) (a) after a prolonged heat treatment (> 1 h) at 1173 K and (b) after 1 h at 1173 K.

cedure having a mean particle size of 5.7 nm. Detailed analysis of the diffraction pattern revealed that a super lattice structure was formed. According to the composition of the catalysts (Pt:Co:Cr = 50:30:20), a cubic or tetragonal ordered structure might be considered. The calculation of theoretical values clearly showed that the observed data match very well with the tetragonal ordered structure (see Table 2). All peaks can be identified, if a tetragonal primitive lattice is assumed. Depending on the average particle size, the peaks are more or less distinctive. Therefore the XRD diagram, Fig. 1a, was used for calculation purposes. The lattice constants of the tetragonal ordered structure are $a_0 = b_0 = 2.6990$ Å and $c_0 = 3.7284$ Å.

The extent of formation of the super lattice structure can be seen from the area percentage of (100) referring to (101). Values smaller than 10% and larger than 15% were assigned to weak and strong, respectively (see Tab. 1). Particularly, if sodium chromate(VI) is used as Chromium precursor, the markedness of the super lattice structure is weak. Furthermore, the lattice contraction of the supported alloy particles increases compared to the lattice constant of 3.925 Å for the face-centred cubic platinum, if the intensity of (100) also increases.

Table 2
XRD data of Pt–Co–Cr alloy catalyst (4)

Miller indices			Interplanar distance for a tetragonal structure		Observed peak intensity (%)
h	*k*	*l*	*d*(observed) (Å)	*d*(calculated) (Å)	
0	0	1	3.7269	3.7284	31.7
1	0	0	2.7021	2.6990	24.9
1	0	1	2.1930	2.1863	100.0
1	1	0	1.9077	1.9085	28.3
0	0	2	1.8616	1.8642	9.8
1	1	1	1.7003	1.6989	12.5
1	0	2	1.5357	1.5339	15.4
2	0	0	1.3489	1.3495	17.3
1	1	2	1.3328	1.3336	12.6

Table 3
Half cell performance of supported Pt–Co–Cr alloy catalysts

Catalyst	O_2 mass activity at 0.9 V (mA/mg Pt) after 3 h	Performance at 200 mA/mg Pt (mV)	
		after 3 h	22 h
1	78	858	839
2	66	852	839
3	68	851	827
4	87	867	845
5	69	852	828
6	41	835	813

Test conditions are as given in the experimental section.

In Table 3 the electrochemical test results for the ORR are summarized. The oxygen mass activity at a potential of 0.9 Volts, measured in mA/mg Pt, and the performance in mV at a current density of 200 mA/mg Pt were given as characteristic data. During start-up phase (3 h), the electrode was conditioned by exposure to open circuit voltage. In order to determine the ageing stability, the electrode was exposed to the above-mentioned conditions for an extended period of time (further 19 h).

The use of only metal nitrates for preparation of catalyst (4) results in the highest initial mass activity values. Even after ageing, the performance of the nitrate-based catalyst (4) is better than those made by the other combinations (see Fig. 2). The reason for the improved performance could be the special preparation method. The simultaneous precipitation of the metal nitrates onto the carbon support allows the co-deposition of small metal hydroxide particles of about 3 nm size, which are in intimate contact to each other. The other preparation methods are adding the non-noble metals after formation of a Pt/C precursor. It is very likely that during thermal treatment diffusion processes for alloy formation will occur differently depending on the catalyst precursor. Recently, a paper [9] describes the higher stability of disordered Pt–Co alloy catalysts compared to the corresponding ordered catalysts. A similar correlation may be found in Table 1, if the mass activity of those catalysts having a less pronounced supper lattice structure (weak or medium) are compared with those examples designated as strong. Of course, the different particle size has to considered so that only catalyst (3) and (4) can be compared with each other.

The preferred disordered alloy catalysts mentioned in that paper [9] were prepared by heating an ordered Pt–Co alloy catalyst for 15 min at 1073 K. In contrast to that, more or less ordered alloy catalysts already after 1 h at 1173 K for the Pt–Co–Cr system were obtained described here. Temperature dependant XRD study of Pt–Co–Cr catalyst (4) showed that all the metal particles were X-ray amorphous at ambient temperature. Upon thermal treatment sharpening of alloy peaks was observed. The diffraction peaks assigned to super lattice planes such as (100), (001) occurred first after cooling down to about 873 K. The period of thermal treatment of the co-deposited metal nitrate precursors at temperatures above 873 K determines mainly the alloy particle size along

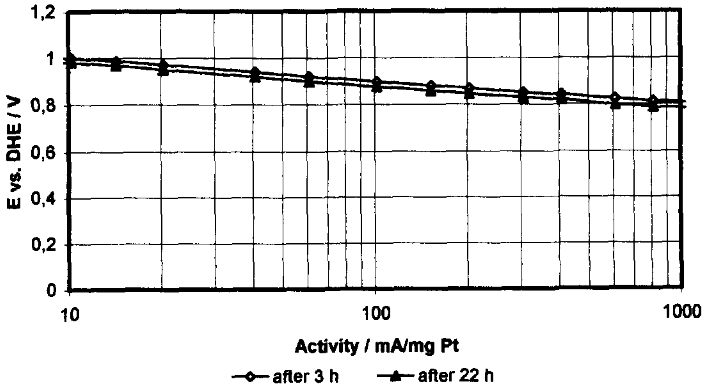

Fig. 2. Hall cell performance of catalyst (4).

with the extent of the formation of the super lattice structure. Further work is necessary to investigate the role of the chromium as well as the associated catalyst preparation method in order to find a conclusive explanation for this different catalyst behaviour.

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