BIFUNCTIONAL ELECTRODE FOR FUEL CELLS

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We were prepared five samples of electrocatalyst by a chemical reaction of the potassium permanganate and the carbon black. These samples were doped, except for one, by the salts of divalent Mn, Mg, Ni and Zn metals.

An attempt was done at first, to estimate the catalytic activity of prepared samples by the measuring of hydrogen peroxide decomposition on 10mg catalyst (PTFE free) and determination of a reaction rate. All our materials exhibited catalytic activity for this reaction. Unfortunately, the results were rather unaccurate due ti very high reaction rate- That is why we can treat the results only for rough orientation.

The apparent reaction rate was dependent on the element used for material doping and it decreased in the series of dopants as follows:

$$Mg^{2+} > \text{without dopant} > Ni^{2+} > Mn^{2+} > Zn^{2+}$$

In the next step, the cyclic voltammetry by the 10mV/s, 5mV/s, 1mV/s, 500μV/s, 200μV/s and 100μV/s scan rate was used. The potential range was from -0,07 to -0,57V against SCE. The obtained data were processed by the wave log analysis and the convolution techniques from the GPES package in order to separate convention controlled reduction of O_2 and solid-state diffusion of intercalated hydrogen. The height of the intercalation peak is increasing when the scan rate is increasing while catalyst wave is approximately constant in all scan rates. We were able to separate both processes in this way. Moreover, we measured voltammograms in systems containing air or only nitrogen. The reduction of O_2 was suppressed in the latter case.

The example of voltammetric curves in air and nitrogen obtained on sample doped by Mg and at scan rate 1 mV/s is given in Fig. 1.

If manganese oxide was prepared without any reduction agent, then the low – valence should be formed by other particles than Mn(2+). To our opinion, hydrogen or hydroxonium ions (H_3O^+) and the hydrogen bridges participate on their formation. Contrary to this, ions of divalent ions added as dopants enter the lattice sites enter the sites for lower valence cations, as the manganese oxide is somewhat similar to the spinels. The highest degree of saturation of these sites should be expected in the presence of Mn^{2+} salts in stoichiometric amounts; under circumstances this salt acts as a reducing agent simultaneously.

The highest charge if intercalation process was found just on the samples prepared without addition of any other salts. The intercalation of hydrogen is perhaps no foreign substance and the movement of hydrogen ions (most likely just as hydrogen bridges) should be very easy. Infortunately, this process is not stable and its charge diminishes in subsequent cycles.

On contrary, the lowest intercalation capacity has been found on material prepared with the addition of Mn^{+2} salt. Highest occupation of free sites or tunnels by manganese ions results in lowest hydrogen capacity, which should be rather stable.

In accordance to that, we observed the decrease of hydrogen intercalation capacity (see Tab. 3) in the series

undoped > Zn > Ni > Mg > Mn

The ionic radius of the ions does not play any clear role.

By the investigation of voltammograms and their convolution analysis, similar conclusions can be drawn. The catalytic activity of the oxides was appraised from the position of the half – wave potential of the oxygen reduction, the value of which was obtained by logarithmic analysis of the current – voltage profile. According to it, the oxide prepared without any divalent doping ions was found to be most active, i.e., the half – wave potential was most positive. On contrary, Mn and-or Mg doped materials exhibited most negative half – wave potential, thus indicating lowest catalytical activity. The convolution analysis of the intercalation peak offered almost similar results.

Also the peak height of convolution waves was in almost identical order.

If the intercalation current was subtracted from the total current, the values of apparent coefficient slightly increased and their scattering narowed (see Tab. 2 a 3)

On contrary to this, the reaction rate of H_2O_2 decomposition yielded in results, which differ from those, mentioned above. It seems probable therefore that both processes proceed under two different reaction paths. It seems possible than the reduction of oxygen does not involve any reaction of hydrogen peroxide as an intermediate. We therefore consider the reaction scheme as follows:

$MnO_2 + H_2O + e^- \rightarrow MnOOH + OH^-$

$O_2 \rightarrow 2\ O_{ads}$

$2\ MnOOH + O_{ads} \rightarrow MnO_2 + 2\ H_2O$

We must have in mind that MnOOH is not any defined entity, but rather a structural unit of an intercalation or insertion substance and we should name it as $MnO_{2-y}(OH)_y$ rather. This has not beendone in here for simplicity.

Table 1. *The parameters obtained by the logarithmic analysis of polarization curves, which were obtained at slowest scan rate and by subtraction of curves measured in nitrogen (considered as background current) from those measured with air.*

Material	$E_{1/2}$ [vs.SCE, V]	I_{max} [µA]	α·n[-]
C+MnOx no additives	-0,131	97,96	3,108
C+MnOx+Mg	-0,178	151,5	2,68
C+MnOx+Mn	-0,172	133,4	2,521
C+MnOx+Ni	-0,150	76,1	2,895
C+MnOx+Zn	-0,145	86,1	3,055

Table 2. *The parameters obtained by the logarithmic analysis of the curves obtained by the convolution analysis. Again, the differences between air and oxygen curves are considered.*

Material	$E_{1/2}$ [vs.SCE, V]	I_{max} [$C \cdot s^{-1/2}$]	α·n [-]
C+MnOx no additives	-0,135	1,47 · 10-3	2,165
C+MnOx+Mg	-0,188	2,93 · 10-3	1,878
C+MnOx+Mn	-0,193	2,85 · 10-3	1,418
C+MnOx+Ni	-0,178	1,54 · 10-3	2,065
C+MnOx+Zn	-0,155	1,74 · 10-3	1,969

Table 3. *The charge corresponding to intercalation of hydrogen (by integration software) on nitrogen saturated electrodes*

	C+MnOx+Zn	**C+MnOx+Ni**	**C+MnOx no additives**	**C+MnOx+Mg**	**C+MnOx+Mn**
Scan rate [Vs^{-1}]	**Charge [C]**	**Charge [C]**	**Charge [C]**	**Charge [C]**	**Charge [C]**
0,01	2,58E-02	8,08E-03	1,11E-01	1,54E-02	3,37E-03
0,005	3,27E-02	1,30E-02	8,38E-02	1,43E-02	6,22E-03
0,001	2,90E-02	2,19E-02	5,67E-02	1,41E-02	9,75E-03
0,0005	2,61E-02	2,27E-02	2,88E-02	1,28E-02	1,08E-02
0,0002	2,51E-02	2,13E-02	2,43E-02	1,27E-02	8,18E-03
0,0001	2,65E-02	2,01E-02	2,30E-02	-	8,86E-03
ø Charge	**2,75E-02**	**1,78E-02**	**5,46E-02**	**1,39E-02**	**7,86E-03**

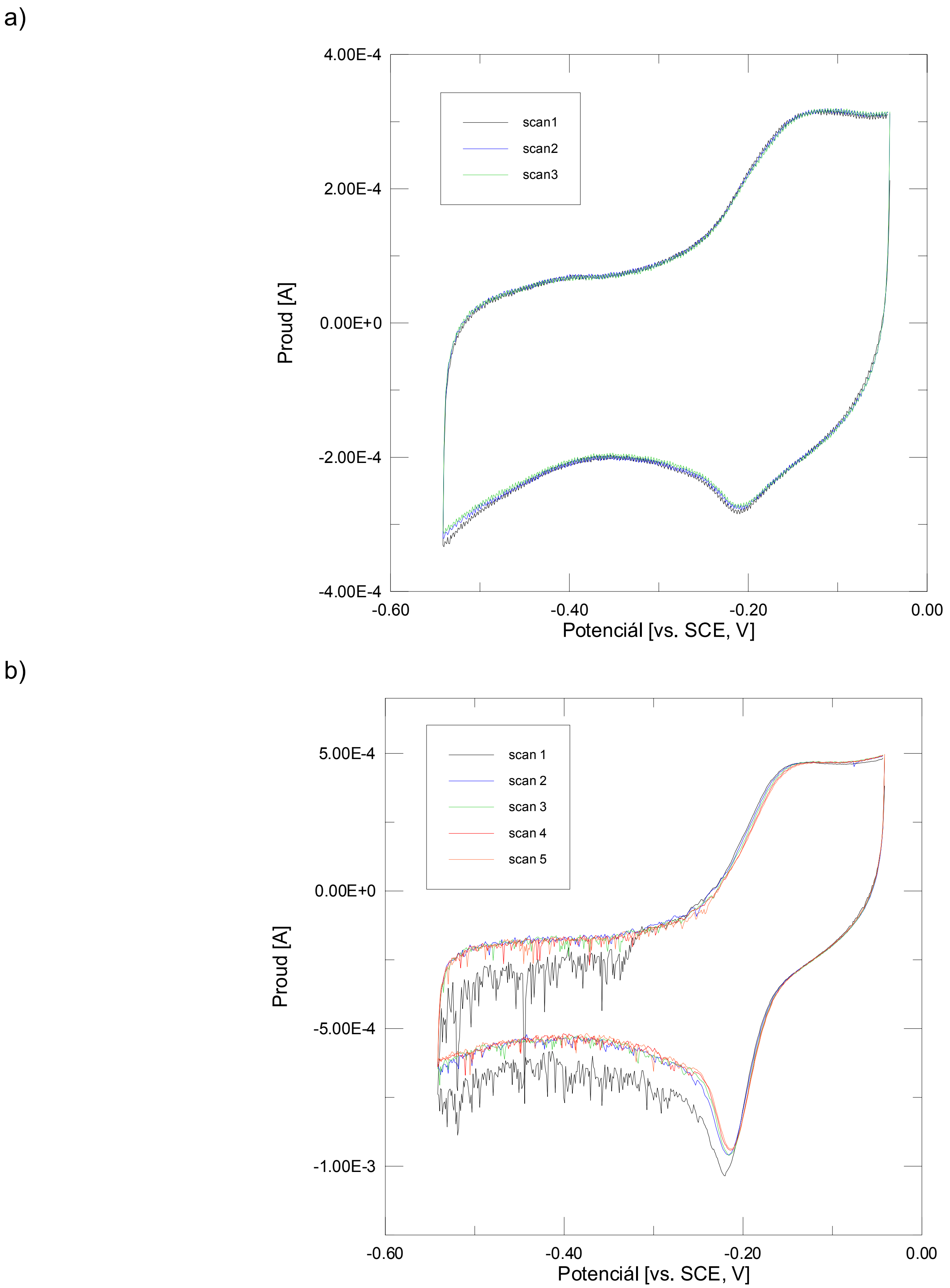

Fig. 1. Voltammetric curves of C+MnOx+Mg at scan rate 1mV/s

a) In nitrogen

b) In air