KINETICS OF OXYGEN REDUCTION IN SODIUM (HYDROXIDE + BOROHYDRIDE) ELECTROLYTE

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Introduction

The increasing demand for portable electronic devices stimulates the need for efficient, clean and high energy-density power sources, among which fuel cells are of great interest, thanks to their high energy density. Using a liquid fuel to replace hydrogen has many advantages in term of fuel cell system simplicity, mass and volume and for safety reasons [1]. However, liquid fuels usually suffer two major drawbacks: their oxidation kinetics is slow and they diffuse through the ion-exchange membrane to the cathode side of the fuel cell, altering the oxygen reduction kinetics, as observed for the direct methanol fuel cell [2-3,4,5].

Amendola first showed the interest of the tetrahydroborate anion (BH_4^-) direct oxidation in a fuel cell anode instead of hydrogen [6]. The anode compartment of the so-called Direct Borohydride Fuel cells (DBFC) is fed with a strong alkaline (pH ≈ 14) solution of sodium borohydride, such species undergoing spontaneous decomposition for pH < 12 [7-8,9,10,11]. The recent development of anion-exchange membranes [12-13], driven by the detrimental cost of most cationic membranes and the possible use of non-platinum (cost-friendly) electrocatalysts for alkaline air-cathode without performances losses [14], increases the interest in the DBFC [15]. However, using an anion-exchange membrane does not prevent the fuel (BH_4^-) crossover down to the cathode compartment, and the development of selective cathode electrocatalysts to perform the oxygen reduction reaction (ORR) in the presence of non-negligible borohydride concentration might be useful, if not mandatory.

In this paper, we investigate several classical ORR electrocatalysts towards the ORR in the presence of non-negligible amounts of borohydride in solution.

Experimental

The oxygen reduction electrocatalysts were 10 wt% Pt/C, Au/C and Ag/C all originating from E-Tek, or 20 wt% manganese oxide-based nanoparticles supported on CHEZACARB carbon powder (CHEMOPETROL Co., Czech Republic), either doped by magnesium cations (2.9 wt% Mg [16]) or undoped.

All the electrocatalysts were characterized as active layers deposited on a glassy carbon electrode (0.196 cm^2) as detailed elsewhere [17]. ORR selectivity experiments were undertaken at room temperature in 1 M NaOH containing 10^{-2} M $NaBH_4$, in parallel to benchmark ORR experiments in pure NaOH. The four-electrode electrochemical cell was connected to a numeric potentiostat, VMP2Z (Biologic), the reference being a mercury/mercuric oxide electrode; all potentials are however expressed versus the normal hydrogen electrode (NHE). The number of electrons exchanged per oxygen molecule was determined at the limiting current density plateaus, using the Levich equation [18].

Results and discussion

Oxygen reduction in sodium hydroxide

The quasi-stationary oxygen reduction voltammograms (Figure 1-a) show the classical RDE diffusion-convection limiting plateaus. They correspond to a 2-electron ORR mechanism for Au/C and a 4-electron ORR mechanism for Pt/C, yielding hydrogen peroxide [19] and hydroxide ion formation respectively. The lower ORR onset for Au/C than for Pt/C (0.050 V vs. NHE vs. 0.230 V vs. NHE) reveals Pt/C higher ORR activity [20]. The Tafel plots corrected from the diffusion in solution using Levich's theory (figure 1-b) also display Pt/C better ORR activity than Ag/C and Au/C, notably in term of current density measured at -0.400 V ORR overpotential (table 1). The first Tafel slopes (b_1), -0.051, - 0.056 and -0.081 V dec^{-1} for Au/C, Ag/C and Pt/C respectively, correspond classical values assuming the Damjanovic mechanism [21-22].

Table 1 *ORR kinetic parameter in 1 M NaOH without/with 10^{-2} M $NaBH_4$; the Tafel slopes marked with $^{(*)}$ are not well-defined on the voltammograms*

Electrocatalyst	1 M NaOH			1 M NaOH + 10^{-2} M $NaBH_4$		
	i_{-400} / A cm^{-2}	B_1 / V dec^{-1}	b_2 / V dec^{-1}	i_{-400} / A cm^{-2}	b_1 / V dec^{-1}	b_2 / V dec^{-1}
Ag/C	$2.6\ 10^{-4}$	-0.056	-	-	-	-
Au/C	$1.3\ 10^{-4}$	-0.051	-	-	-	-
Pt/C	$1.5\ 10^{-2}$	-0.081	-	-	-	-
MnO_x/C	$4.0\ 10^{-3}$	-0.038	-0.16^{*}	$2.6\ 10^{-3}$	-0.033^{*}	-0.130
MnO_x-Mg/C	$3.3\ 10^{-3}$	-0.039	-0.18^{*}	$1.5\ 10^{-3}$	-0.031^{*}	-0.160

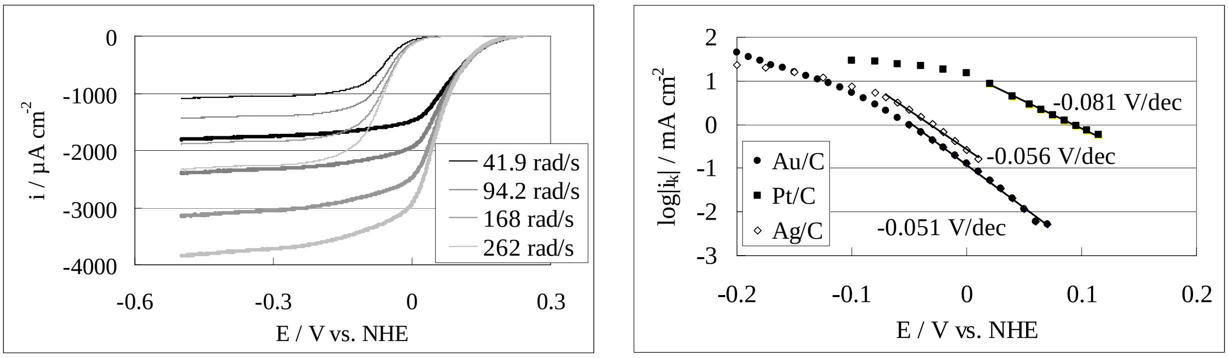

Figure 1 *ORR voltammograms (1 mV s^{-1}) plotted on Pt/C (bold) or Au/C (thin) in 1 M NaOH (a) and corresponding Tafel plots (b)*

Figure 2-a shows both MnO$_x$/C-based electrocatalysts display rather similar ORR wave onset; the limiting current plateaus yield 2.3 and 3.2 electrons per oxygen molecule for MnO$_x$/C and MnO$_x$-Mg/C respectively. Figure 2-b confirms both materials close kinetic activity, while the similar Tafel slopes at low ORR overpotential reveal they reduce oxygen with the same reaction mechanism (at low overpotential), which makes us think that the ORR path changes for MnO$_x$/C according to the electrode potential.

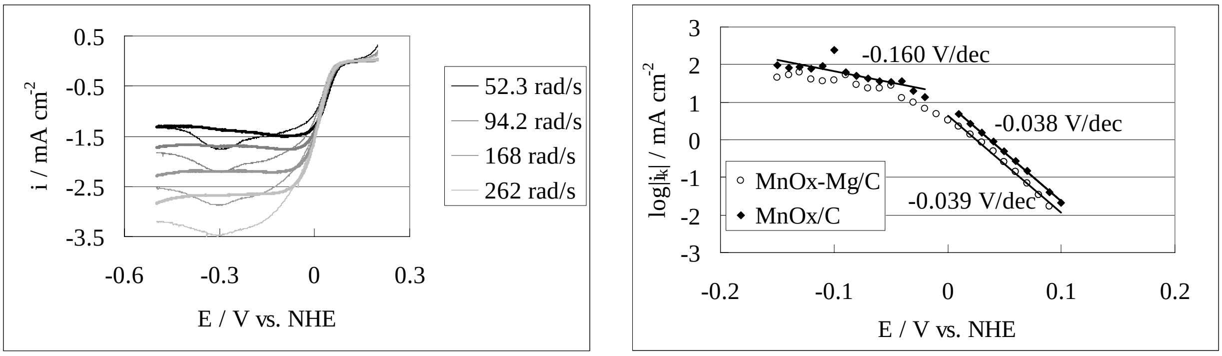

Figure 2 *ORR voltammograms (1 mV s^{-1}) plotted on MnOx/C (bold) or MnOx-Mg/C (thin) in 1 M NaOH (a) and corresponding Tafel plots (b)*

The manganese-oxide materials exhibit an ORR activity in 1 M NaOH close (but inferior) to that of Pt/C. The ORR activity for the various materials varies in the sequence:

$$\text{Pt/C} > \text{MnO}_x\text{-Mg/C},\ \text{MnO}_x\text{/C} > \text{Ag/C} \geq \text{Au/C}$$

Pt/C being the best electrocatalyst in 1 M NaOH without strong reducer (BH$_4^-$) in solution.

In the presence of 10-2 M sodium borohydride

Upon sodium borohydride addition in solution (10^{-2} M), the open-circuit potential for a carbon-supported platinum electrode dramatically falls down to around -0.8 V vs. NHE (it was ~0.2 V vs. NHE in the absence of borohydride). Such decrease evidences the creation of a mixed potential at the platinum electrode and renders Pt/C really not suited as cathode electrocatalyst (for a DBFC). Despite Au/C weaker activity towards BH$_4^-$ hydrolysis reaction [23-24] and rather good ORR activity (table 1, figure 3), Au/C are not suited either for a DBFC cathode: with 10^{-2} M sodium borohydride in solution, the ocp for Au/C fall down below -0.35 V vs. NHE, rendering the gold electrocatalyst useless towards the ORR. The tetrahydroborate oxidation, rather fast for Au/C [25], competes with the oxygen reduction. Ag/C do not display better ORR selectivity; the oxygen reduction only starts to be quantitative below -0.3 V vs. NHE, a high oxidation current being monitored above this value.

The behaviour of MnO_x/C-based electrocatalysts in the presence of sodium borohydride in solution sharply differs from those for Ag/C, Au/C and Pt/C. First, the open-circuit potential decreases only from 0.075 and 0.050 V for MnO_x/C and MnO_x-Mg/C respectively upon the presence of 10^{-2} M BH_4^- in solution (the ocp decrease exceeded 0.3 V for the other materials). Moreover, the voltammograms from Figure 3-a show ORR waves barely altered by the presence of sodium borohydride, at least above 0 V vs. NHE. The ORR onset remains almost unchanged with or without tetrahydroborate anion in solution, which signs the manganese oxide-based electrocatalysts tolerance to sodium borohydride. The number of electrons exchanged at the limiting plateaus remains unchanged for MnO_x/C (n = 2), while it decreases from n = 3.2 to n = 2 with borohydride in solution for MnO_x-Mg/C. Both manganese oxide-based materials reduce oxygen according to the same reaction scheme when tetrahydroborate anion is present in solution. This further means the presence of BH_4^- in solution modifies the ORR path for MnO_x-Mg/C. Such effect is seen for both materials on the Tafel representation of the kinetic current densities (Figure 3-b), which indicates that the Tafel slope has changed from around -0.040 V dec^{-1} in sodium hydroxide to around -0.130 to -0.160 V dec^{-1} in the presence of sodium borohydride. The strong reducer BH_4^- could displace the $Mn^{IV} \leftrightarrow Mn^{III}$ equilibrium at the surface of the MnO_x nanoparticles towards the formation (and stabilization) of Mn^{III} species, the re-oxidation of which is normally (in the absence of BH_4^-) concomitant with the oxygen reduction.

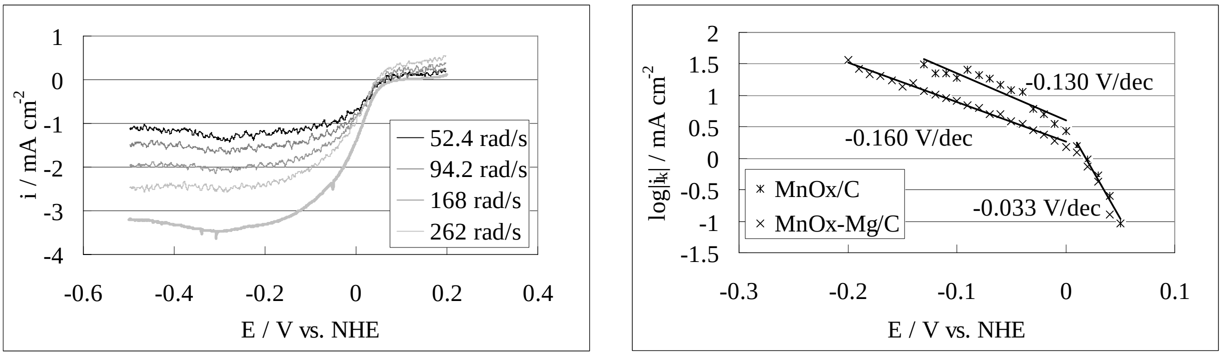

Figure 3 *ORR voltammograms (1 mV s^{-1}) plotted on MnOx-Mg/C (thin) in 1 M NaOH with 10^{-2} M $NaBH_4$; benchmark voltammogram without $NaBH_4$ (bold) (a); Tafel plots relative to the ORR voltammograms on MnO_x/C and MnO_x-Mg/C in 1 M NaOH + 10^{-2} M $NaBH_4$*

In term of reaction kinetics, the effect of sodium borohydride is small: the current density measured at -0.400 V ORR overpotential only decreases by a factor of 2 compared to the pure sodium hydroxide solution (table 1). We point out that the results for Ag/C, Au/C and even more Pt/C were so dramatically bad, that the reaction kinetics in the presence of sodium borohydride rendered any calculation of i_{-400} hopeless: at 0 V vs. NHE, the current measured on these materials is indeed still an oxidation current. As a result, only manganese oxide-based electrocatalysts are able to sustain the presence of non-negligible amounts of sodium borohydride, while still remain active towards the ORR in the potential window relevant for use in a DBFC cathode. Their only drawback would follow the reaction path in the presence of sodium borohydride, probably involving the production of hydrogen peroxide, both for MnO_x/C and MnO_x-Mg/C. We point out that hydrogen peroxide formed should be reduced by the tetrahydroborate ion in solution, thus decreasing their lifetime.

Conclusion

We studied the ORR selectivity in the presence of BH_4^- in 1 M NaOH for various electrocatalysts. Whereas Pt/C ORR activity is the highest in pure sodium hydroxide, Pt/C is not usable with traces of sodium borohydride in solution following its ocp and ORR wave onset sharp decrease below reasonable potentials values. Such bad effect of sodium borohydride is less dramatic for Ag/C and Au/C, following their lower BH_4^- hydrolysis activity, but they still cannot be used as DBFC cathode electrocatalyst. Finally, only MnO_x-based electrocatalysts seem rather unaffected by the presence of sodium borohydride in solution. Their ocp is only mildly shifted negative, while their ORR activity in the presence of 10^{-2} M sodium borohydride is barely lower (by a factor 2) compared to pure NaOH solutions. From this kinetics point of view and assuming tetrahydroborate anion crossover will not be zero in an operating DBFC, manganese oxide-based materials are suitable electrocatalysts to be used in DBFC cathodes.

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