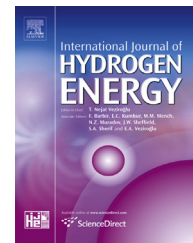




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Oxygen evolution in alkali with gas diffusion electrodes

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ABSTRACT

Progresses in the area of the oxygen evolution reaction (OER) are now occurring at a much faster rate relative to few years ago. For this reason, it has been deemed appropriate to present a critical review of the major and most recent contributions towards a fundamental understanding of what determines the OER electrocatalytic properties of a material. Furthermore, the technologies used to produce practical OER electrodes with top activities are assessed and the current benchmarks of performance are identified. Furthermore, results pertaining to our work on Raney–Ni gas diffusion anodes, which have been optimized in thickness and composition, are presented. An addition of 10 wt.% of a Co₃O₄ micrometric powder as co-catalyst (with Raney Ni–Fe) was found to enhance the polarization behavior and performance. The electrode so obtained achieves activities comparable with those of the best electrodes reported in the literature.

Great emphasis has been placed in the analysis of the stability of the prepared Gas Diffusion Electrodes. Most of the GDEs were found to be stable in weeks long experiments with intermittent operation. The issue of integrating several functional layers (gas diffusion layer, active layer with current collector, separator layer) within a single, mechanically strong electrode assembly is briefly addressed.

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1. Introduction

The oxygen evolution reaction (OER) is a very complex, multi-steps, multi-electrons phenomenon of paramount importance for biological systems (e.g. photosynthesis) and applied electrochemistry. A better understanding of OER is now being pursued by concurrent theoretical and experimental studies, and by developing electrodes specifically conceived to address fundamental issues. OER usually gives the major contribution

to power losses in energy intensive processes such as electrical or solar water splitting and rechargeable metal–air batteries due to the sluggish nature of the electrode kinetics. This is the reason for which an empirical search for the “best” OER electrocatalyst in base and/or in acid has been vigorously conducted for decades. While platinum is usually considered the benchmark for hydrogen evolution in acidic environment, the situation is less defined for OER. In an effort to establish an OER benchmark, Lee et al. [1] compared the OER activities in

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acid and base of nanoparticles of rutile IrO_2 and RuO_2 with similar morphologies. For an overpotential of 30 mV both oxides have a current density of $\sim 20 \text{ mA cm}^{-2}$ in 0.1 M HClO_4 and of $\sim 10 \text{ mA cm}^{-2}$ in 0.1 M KOH. For lower overpotentials the performances of RuO_2 are better.

A paper by Minguzzi et al. [2] explores the pH dependence of the polarization curves of some of the best known OER catalysts; the resulting dynamic potential–pH diagrams represent the activities as function of pH and potential, and provide a comprehensive comparison of different OER catalysts and of the pH–potential regions where their top activity is attained. Quite surprisingly, the reputed “best” OER catalyst in acid, IrO_2 , actually reaches its highest activity at pH = 14 (100 mA cm^{-2} with E vs. Hg–HgO $\sim 835 \text{ mV}$ or $\eta \sim 531 \text{ mV}$) where, however, even higher turnover frequencies are recorded for Co_3O_4 [2]. The result is not inconsistent with those reported by Lee et al. [1], who explored just the low current side of the polarization curves; furthermore it is strongly supported by an important paper by Suntivich et al. [3], who introduced a rational method to design metal oxides as OER catalysts. The method is based upon identification of a “descriptor” related with the intrinsic properties of a material which control catalysis. The classic descriptor for hydrogen evolution on a metal (M) surface is the H–M bond strength introduced by Trasatti forty years ago [4] which has an optimal value when the exchange current attains a maximum (volcano plot). Finding a good descriptor for OER is much more complex due to the difficulty of a chemical reaction involving several sub-reactions and many intermediates. From a systematic analysis of ten La–based transition metal oxides with the perovskite structure, Suntivich [3] inferred that the appropriate descriptor is the number of occupied *d* orbital states with e_g symmetry, and backed this conclusion with DFT calculations showing that this descriptor is related with the oxygen adsorption energy. Furthermore, the paper identified from first principles a mixed oxide, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, as being at the top of the volcano plot and confirmed experimentally that this compound has a specific activity more than one order of magnitude higher than IrO_2 .

The conclusion of Minguzzi [2] concurs also with the findings of Yeo and Bell [5] who found that the OER turnover frequency of a monolayer of Co_3O_4 deposited on a gold support surpasses that of IrO_2 . *In situ* Raman spectroscopy reveals that such a high activity is related with the fraction of Co^{IV} cations within the monolayer, and that this fraction increases with the electronegativity of the support (higher for Au and progressively lower for Pt, Pd, Cu, Co). The same authors give also an important contribution to the understanding of the role of the different phases of the Ni oxy–hydroxides in the OER activity of Ni electrodes, which have a great practical importance [6]. It is well known that layers of NiOOH form on the surface of a Ni electrode at potentials where OER begins. Yeo et al. [5] gave Raman evidence that electrochemical cycling in the potential region $0 \div 0.8 \text{ V}$ vs. Hg–HgO (in 0.1 M KOH) transforms the original γ NiOOH phase into the three times more active β NiOOH phase that contains a higher $\text{Ni}^{\text{III}+\delta}$ oxide which is stable above 0.52 V vs. Hg–HgO and favors OER. The relevance of this result is enhanced by the conclusion of a paper by Subbaraman et al. [7] who compared the OER activities of $3d$ –M–hydro(oxy)oxides (M = Mn, Fe, Co, Ni) and found

out that their OER activity is inversely related with the strength of the OH– M_x ($2 \leq x \leq 2.6$) bond strength, which is highest for Mn and lowest for Ni. The computational approach to electrocatalyst selection is gaining grounds by the day. Man et al. [8] identified SrCoO_3 as the best catalysts among simple perovskites and suggested that a suitable descriptor for the OER is the difference between the calculated free energy of reaction ΔG_0 of the second and the first electron abstraction step ($\Delta G_0\text{O}^* - \Delta G_0\text{HO}^*$), a quantity which describes correctly the experimental trends from the literature. These DFT computations also suggested that cobalt oxide is more reactive than RuO_2 , a result supported by the above mentioned results [5,6] but not by older data of Co_3O_4 activities, with excess oxygen being a possible reason for the discrepancy. Rossmel et al. [9,10] performed DFT studies of the rutile-type oxides (TiO_2 , RuO_2 , IrO_2) and Mn clusters in photosystem II assuming that the reaction in acid begins with formation of an O–O bond between one surface transition metal oxo–group (TM = O) and one water molecule. By comparing the reactions of water splitting in biological and electrochemical systems, they showed that ruthenium oxide is the best material among the inorganic compounds investigated, but demonstrated also that the Mn clusters of photosystem II are more efficient than RuO_2 towards OER and made an early prediction about the existence of even better systems.

Among the most recent and relevant works which contribute experimentally to the quest of the best OER catalyst we may quote a work from Chou et al. [11] where similar nanoparticles of different cobalt oxides were compared and shown to be able to attain, at pH = 14 and for 1 mg cm^{-2} catalyst loading, a current density of 100 mA cm^{-2} at E vs. Ag–AgCl $\sim 575 \text{ mV}$ or $\eta \sim 370 \text{ mV}$). Another work by Yin [12] bridges the gap between homogeneous and heterogeneous catalysis (and between natural and artificial photosynthesis) reporting formation by self-assembly in water of a stable complex $([\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-})$ comprising a Co_4O_4 core which acts as a water oxidation catalyst stabilized by polytungstate ligands with catalytic turnover frequencies for O_2 production of more than 5 s^{-1} at pH = 8. Finally, Liang et al. [13] found unexpected synergetic coupling effects between nitrogen doped graphene and Co_3O_4 nanocrystals deposited on it. This system turns out to be an oxygen reduction catalyst as effective as Pt in alkali (but much more stable); also, its OER activity is substantial, attaining 10 mA cm^{-2} at room temperature in 1 M KOH with an overvoltage of 310 mV. To our knowledge, this is the best bi-functional ORR–OER electrode without Platinum Group Metal (PGM) catalysts.

The research summarized above has much advanced our general understanding of OER through a combination of sophisticated tools (theoretical and experimental) and synthesis of new exotic materials. However much progress has also been made in developing traditional and better known materials mostly, but not uniquely, based upon Co and/or Ni oxides, which are often perceived as being now very close to technological exploitation. Chien et al. [14] prepared NiCo_2O_4 aerogels which attained, at 25°C and in 1 M KOH, a current density of 100 mA cm^{-2} at an overpotential of only 184 mV. This compound was previously prepared in other laboratories following different recipes, which led to substantially less performing catalysts. The question, not addressed by these

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