

Bifunctional oxygen/air electrodes

Ludwig Jörissen

Zentrum fuer Sonnenenergie und Wasserstoff-Forschung Baden-Wuerttemberg, Geschäftsbereich 3, Elektrochemische Energiespeicherung und Energiewandlung, Helmholtzstr. 8, D-89081 Ulm, Germany

Received 18 March 2004; accepted 10 May 2004

Available online 15 December 2005

Abstract

A selective review on the materials and construction principles used for bifunctional oxygen/air electrodes is given. The discussion emphasizes the catalytically active materials used for the construction of these electrodes, which are a key component in electrically rechargeable air breathing electrochemical systems. Whereas, in acid electrolytes normally noble metal catalysts must be used, there is a possibility to use less expensive transition metal oxides in alkaline electrolytes. Typical transition metal oxides have the perovskite, pyrochlore and spinel structure. © 2005 Elsevier B.V. All rights reserved.

Keywords: Bifunctional oxygen electrode; Electrochemical oxygen reduction; Oxygen evolution; Reversible fuel cell

1. Introduction

Bifunctional oxygen/air electrodes are a prerequisite for the development of electrically rechargeable metal/air batteries and/or so called regenerative fuel cells. Bifunctional oxygen/air electrodes consume oxygen during electricity generation (e.g. battery discharge, fuel cell operation), whereas, oxygen is evolved during battery charge or electrolysis mode.

Air based battery systems stand out for their high specific energy since only the negative active mass must be stored in the battery while the reactant for the positive electrode is taken from the ambient air. Table 1 shows the characteristic data of different metal–oxygen cells.

From the metals shown in Table 1, Li, Ca, Mg, and Al systems can only be operated as a primary system in an aqueous environment. Zn, Fe, Cd and metal hydride electrodes can be charged electrically in an aqueous electrolyte. Cd–air systems will most probably not be used in vehicle size batteries due to the high toxicity of Cd. Typically aqueous alkaline electrolytes are used in metal air batteries due to the better performance of the oxygen electrode and the reduced cor-

rosion of the metal electrodes in the alkaline environment. Nevertheless, progress in the development of fuel cells and electrolyzers involving acid polymer membranes makes the development of reversible polymer membrane fuel cells an interesting option for energy storage. In principle, metal air cells can also be used as oxygen sensors.

2. Oxygen electrochemistry

It is well known that the electrochemical reaction kinetics of oxygen is generally rather slow. Although it may appear simple on a first glance, the electrochemistry of oxygen is rather complicated to describe due to its strong irreversibility. In the following table the standard electrode potentials of reactions involving oxygen in different electrolytes are given (Table 2).

The reversible potentials of oxygen electrodes are difficult to measure, since the reactions involved are dependent on many factors such as the electrolyte and the surface chemistry of the catalyst used. Oxygen electrochemistry and their applications were reviewed in more detail in [3–5] Furthermore, a chapter has been devoted to various aspects of the oxygen reduction/evolution reaction in the handbook of fuel cells [6]. Oxygen reduction can occur via two generally different pathways the so-called direct four-electron reduction

E-mail address: Ludwig.joerissen@zsw-bw.de.
URL: <http://www.zsw-bw.de>.

Table 1
Characteristic data of metal–oxygen cells

Metal anode	Electrochemical equivalent of metal [Ah kg ⁻¹]	Theoretical cell voltage with O ₂ electrode [V]	Theoretical specific energy of metal oxygen couple [Wh kg ⁻¹]	Practical operating voltage [2] metal–oxygen [V]
Li	3861	3.3	12741	2.4
Ca	1337	3.4	4547	2.0
Mg	2205	3.1	6837	1.4
Al	2980	2.7	8046	1.6
Zn	820	1.6	1312	1.1
Fe	960	1.3	1248	1.0
Cd	478	1.2	572	0.9
H ₆ LaNi ₅	367	1.2	440	0.8

Data calculated from [1].

Table 2
Standard electrode potentials of selected oxygen reactions in aqueous electrolytes at 25 °C [3].

Electrochemical reaction	E_0/V vs. SHE
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.695
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.401
$O_2 + H^+ + e^- \rightarrow HO_2$	-0.053
$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	-0.065
$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$	-0.133
$O_2 + e^- \rightarrow O_2^-$	-0.284

as well as a pathway involving peroxide giving rise to the following overall reactions [3,7] as shown in Table 3.

The peroxide path is favored on graphite and most other carbons, oxide covered metals such as Ni or Co and some transition metal macrocycles. A large number of detailed reaction mechanisms involving specific catalytic sites were described in the literature and summarized in [3,6]. The following catalyst materials favor the two-electron reduction path to peroxide [6]:

- Mercury.
- Gold (except gold (1 0 0) in alkaline solution [8]).
- Carbon.
- Oxide covered metals.
- Most transition metal oxides.

The so-called direct four-electron reduction generally involves a sequence of steps, sometimes involving even an

Table 3
Possible reaction pathways for oxygen reduction in alkaline and acidic media

	Reaction	E_0/V vs. SHE
Direct four-electron pathway		
Alkaline solution	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.401
Acid solution	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229
Peroxide pathway		
Alkaline solution	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	-0.065
Peroxide reduction	$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$	0.867
Peroxide decomposition	$2HO_2^- \rightarrow 2OH^- + O_2$	-
Acid solution	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.67 V
Peroxide reduction	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.77 V
Peroxide decomposition	$2H_2O_2 \rightarrow 2H_2O + O_2$	-

adsorbed peroxide intermediate. This reaction pathway is predominant on noble metal catalysts, some transition metal oxides and some transition metal macrocycles. In the peroxide pathway free H₂O₂ can be detected in the electrolyte, which can be used as an indicator. The H₂O₂ formed in solution can be decomposed either electrochemically or by simple chemical decomposition. Oxygen from the chemical decomposition reaction can immediately react at the electrode. Therefore, four electrons are exchanged in both pathways. The four electron reaction path breaking the O–O bond is favored by the following catalysts [6]:

- Platinum.
- Platinum family metals.
- Platinum alloys.
- Silver.
- Gold (1 0 0) in alkaline solutions [8].
- Metallic iron in neutral solutions [9].
- Some metal oxides (e.g. perovskites, pyrochlores).

On metallic catalysts, oxygen is generally evolved from the corresponding metal oxides, which may be either thin films as in the case of noble metals (Pt, Au, Ir, Rh, Ru) or thick films as in the case of Ag or Ni. Platinum is a rather poor electrocatalyst for oxygen evolution due to the formation of a stable oxide layer. Ruthenium metal, although being a good electrocatalyst for oxygen evolution is strongly corroded. However, bulk noble metal oxides such as RuO₂ or IrO₂ show rather good performance. However, IrO₂ needs to be stabilized by thermal treatment or by doping with Ta. Nickel is widely used as an electrocatalyst for oxygen evolution in alkaline electrolytes. However, at high potentials lower conductivity phases involving Ni⁴⁺ are formed which are reducing the performance. Some transition metal oxides also show good performance in oxygen evolution. This is particularly the case in some spinel type oxides such as NiCo₂O₄.

The reaction pathways involved in oxygen evolution often are rather complex. Mechanisms are also likely to change depending on the electrode potential. On metallic surfaces the rate-determining step is the electron transfer from either H₂O in acid electrolytes or OH⁻ in alkaline electrolytes to form adsorbed OH radicals at the electrode surface. Oxygen evolution from metal oxide surfaces was analyzed in [10,11]. This pathway is leading to the intermediate formation of H₂O₂

where the rate-determining step was found to be the breaking of the surface-OH bond. Another multi-step mechanism for alkaline electrolytes not involving H_2O_2 was proposed by Miles et al. [12]. The rate-determining step was found to depend on the electrode used.

3. Design principles of bifunctional oxygen/air electrodes

Due to the slow kinetics involved in oxygen electrochemistry, porous high surface area electrodes are required to achieve significant current densities. For the oxygen reduction reaction, normally porous gas diffusion type electrodes are used. The porous structure must be optimized as to provide an extended reaction zone at the three-phase boundary between gas, catalyst and electrolyte. In order to optimize the gas access to the catalytically active sites, a rather hydrophobic gas transport pore system must be maintained. Quite often the gas diffusion electrode itself is divided into two layers. The layer next to the electrolyte contains the catalytic active material in a mildly hydrophobic environment having fine porosity, whereas, a highly hydrophobic gas diffusion layer provides bigger gas transport pores. Additionally, a current collector such as a metal mesh or foam or a graphite felt or cloth are incorporated into the gas diffusion electrode.

For oxygen evolution normally porous electrodes sintered on a metallic substrate such as titanium is used. A good example is the so-called dimensionally stable anode widely used in the chlor alkaline industry. Porous, hydrophilic catalyst layers (e.g. mixtures from RuO_2 , IrO_2 and Ta_2O_5) are sintered on a Ti-substrate. Evolving gasses are simply removed by bubble formation.

The function of bifunctional oxygen electrodes generally require the combination of both operating principles. Therefore, hydrophobic catalyzed sites must be present for oxygen

reduction as well as hydrophilic sites for oxygen evolution. Sometimes different catalyst materials can be used for oxygen reduction and oxygen evolution.

Different strategies can be adopted for the construction of an electrically rechargeable metal–air system.

- Use of separate electrodes for O_2 evolution and consumption.
- Use of a multi-layered electrode with separate layers for O_2 evolution and consumption.
- Use of single layered electrodes with a bifunctional catalyst.

Fig. 1 shows several construction principles for bifunctional oxygen electrodes. In version (a), a single catalytic layer is used to carry out both reactions. This construction is relatively simple to manufacture and to integrate into batteries. However, requires the use of highly stable catalyst materials, which must withstand the highly oxidizing conditions upon oxygen evolution as well as the more reducing conditions observed under oxygen reduction at high current density. Such electrodes have been described for use in electrically rechargeable metal hydride–air batteries and in Zn–air batteries [13]. In Fig. 1(b) the separation of oxygen evolution and oxygen reduction into two different layers is shown. This construction offers the possibility of separate optimization of oxygen reducing and oxygen evolving electrodes with respect to performance and stability. However, it adds to the complexity and weight of the system. Electrically rechargeable metal hydride air batteries using separate electrodes have been described in [14]. A double-layered electrode construction is shown in Fig. 1(c) and in more detail in Fig. 2. Here the hydrophilic side for oxygen evolution, which can well have a flooded pore system is facing the electrolyte, whereas, the part used for oxygen reduction is oriented towards the air side. A current collector could be placed between the two functional layers. Such

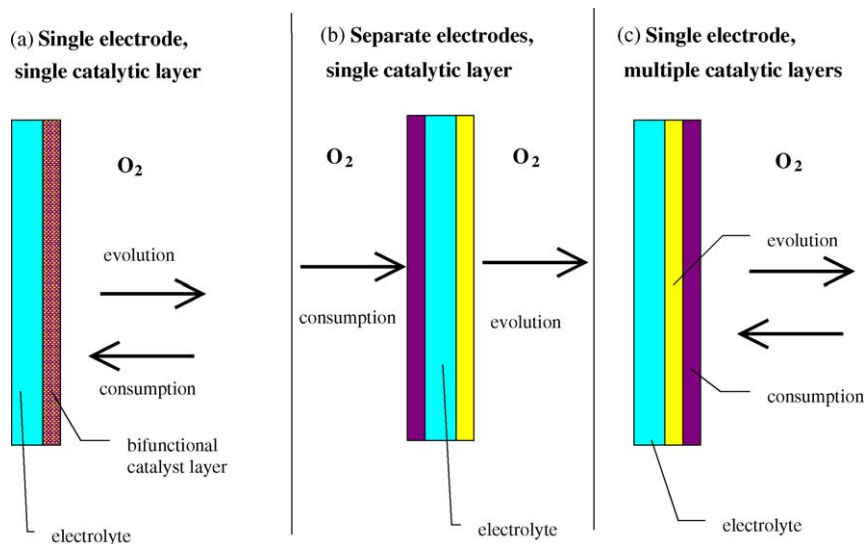


Fig. 1. Construction principles of bifunctional oxygen/air electrodes.

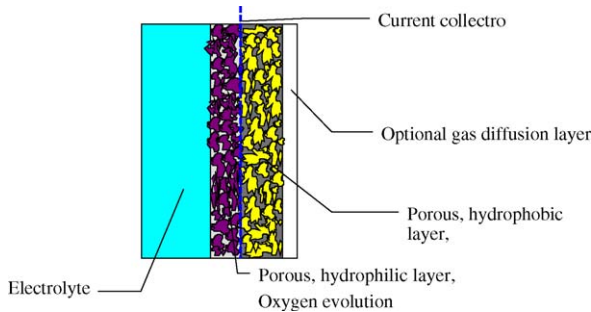


Fig. 2. Possible microstructure of a multi-layered electrode.

electrodes could provide better performance on the expense of higher complexity during manufacturing and possibly increased mass transfer losses. A bifunctional air electrode design using layers of different porosity and hydrophobicity has been described in [15]. The electrode was made from sintered nickel using silver as a catalyst. The electrode consisted of a fine-grained reaction and coarse-grained transport layer. Spacers and hydrophobing agents were used to control the porosity and wettability of the electrodes, respectively. Stability of more than 100 cycles in charge/discharge mode has been achieved.

During charge oxygen is generated in a highly reactive form thus causing highly corrosive conditions to the catalyst as well as to the conductive support material. Particularly, high surface area carbon materials used as conductive support are severely attacked under anodic conditions. Reduced rates of support corrosion have been observed using graphitized carbon materials as conductive support [16].

In multi-layered electrodes the oxygen reduction catalyst is protected by a dual porosity design. Oxidation of the electrode structure during charge is minimized by applying a slight pressure to the gas side thus breaking the electrolytic contact to the “oxygen reduction” part of the electrode [17].

For high power applications, the bifunctional oxygen electrode has to accept rapid changes in its potential imposed by phases of battery discharge during acceleration or cruise followed by charging phases during regenerative braking. Ideally, all components of a bifunctional electrode should withstand these conditions. Therefore, a single layered electrode structure with a true bifunctional catalyst should be the most efficient and cost effective design for an electrically rechargeable metal–air battery.

4. Alkaline systems

Most electrochemical systems using bifunctional oxygen/air electrodes are using an alkaline electrolyte since evolution and consumption of oxygen can be carried out at non-noble metal catalysts. Furthermore, the exchange current densities of oxygen evolution/reduction are higher than in acidic electrolytes. A wide variety of metal oxides have been investigated for use in electrically rechargeable alka-

line fuel cells [18] for application as catalyst and catalyst support.

However, in alkaline systems the air electrodes are sensitive to CO_2 , which is reacting with the OH^- ions to form carbonates. The detrimental effect of CO_2 to the lifetime of bifunctional oxygen/air has been shown [19]. In this study, it was shown that bifunctional oxygen electrodes operated in pure oxygen failed in the oxygen evolution (anodic) mode after approximately 2.500 h. Whereas, oxygen air electrodes operated in CO_2 containing gas failed (CO_2 content below 1.000 ppm) after approximately 250 h in oxygen reduction (cathodic) mode. The CO_2 sensitivity of oxygen gas diffusion electrodes in cathodic mode can be influenced by the choice of the carbon black used [20].

4.1. Noble metal catalysts

Bifunctional air electrodes containing Pd catalyzed porous nickel were investigated [21]. These materials showed acceptable initial performance, however, strong performance decay was observed within 50 cycles most probably due to the loss of Pd. Other noble metal catalysts such as Ag or Pt that show high performance in oxygen reduction are not suitable due to dissolution under conditions of oxygen evolution.

CoIrO_3 and NiIrO_3 have shown reasonable activity for oxygen evolution in a high surface area form. Furthermore, high surface area RhO_2 and IrO_2 show high activity for oxygen evolution. Good activity and stability has also been observed for PbPdO_2 [18].

4.2. Non-noble metal catalysts

Oxygen reduction in alkaline systems does not necessarily require the use of pure noble metal catalysts. Transition metal oxides or mixed transition metal oxides have also been successfully used. A review of non-noble metal catalyst has been given in [22]. Charge–discharge efficiencies above 60%, current densities of 200 mA cm^{-2} and power densities of 1 W cm^{-2} have been claimed [23]. However, only a few materials can catalyze oxygen evolution and reduction simultaneously. The performance of transition metal oxides and mixed transition metal oxides is often limited by their low bulk conductivity and limitations in the active surface area, which can be achieved. Nevertheless, properties such as electronic conductivity or ion mobility in the mixed transition metal oxide crystals can be tailored by their composition.

4.2.1. Perovskite catalysts

Perovskite type oxides have the general formula ABO_3 . Their properties can vary over a wide range depending on the nature of A and B. The cubic perovskite crystal lattice is a rather rugged host for a variety of mixed transition metal oxides. The structure can even adapt distortions from the basic cubic symmetry-giving rise to interesting properties. Substituted perovskites can generally be described by the formula $\text{A}_{1-x}\text{A}'_x\text{B}_{1-y}\text{B}'_y\text{O}_3$.

A wide selection of materials using La and Nd in position A, Sr, Ba, Ca in position A', and Ni, Co, Mn and Ru in position B have been synthesized and shaped into electrodes [24]. Thermal decomposition of nitrates, acetates, oxalates or carbonates was carried out initially followed by a solid-state reaction at temperatures between 600 and 900 °C. The electrodes were made from two layers. In the oxygen reduction layer, a mixture of catalyst and PTFE (25 wt.%) was roll bonded onto an expanded Ni metal sheet. The oxygen evolution layer consisted of Ni powder bonded with 5% PTFE and was placed on the opposite side of the expanded metal. The oxygen reduction layer was backed by an additional PTFE film. In these investigations $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ and LaNiO_3 showed good initial performance. However, their performance deteriorated upon cycling. Admixture of graphite to the oxygen reduction layer improved the electrical and cycling performance dramatically. More than 280 cycles were carried out.

LaNiO_3 was investigated by several groups as a bifunctional catalyst [18,25–27]. It was found to be reasonably stable. However, typical signals for the formation of the $\text{NiOOH}/\text{Ni}(\text{OH})_2$ couple are evident even after short cycling. The performance of the material could be greatly enhanced when it was prepared by the mallic acid method [28,29].

A series of compounds of the type $\text{LaFe}_x\text{Ni}_{1-x}\text{O}_3$ has been investigated as a model compound. Good performance and stability in long term operation are observed for oxygen generation. However, perovskite materials are not very active for oxygen reduction. Degradation effects become prominent after a short time under cathodic operation. Yet, reasonable performance for peroxide decomposition has been observed [30].

The activity of transition metal oxide catalysts can be correlated with the ability of the cations to adopt different valency states, particularly when they form redox couples at the potential of oxygen reduction/evolution [31].

From early studies based on LaCoO_3 [32], it was found that the conductivity of the material could be modified by doping A and B positions of the material while maintaining the perovskite structure. A variety of substituted materials having the perovskite structure were investigated in low area gas diffusion electrodes in order to evaluate their stability with respect to reducing conditions. The effects of substitution on the A and the B site has been investigated [33–35].

Perovskite type oxides of the composition $\text{La}_{1-x}\text{Ca}_x\text{MO}_3$ were synthesized by the amorphous citrate method [36]. Gas diffusion electrodes were prepared by mixing 25–70 wt.% catalyst ($3.5\text{--}9\text{ mg cm}^{-2}$) with carbon black. Carbon black of different surface area was used for the catalytic and the gas supply layer. PTFE (15–25 wt.%) was used as a binder. Teflonized powder mixtures were preformed from suspension, filtered and heated at up to 280 °C. After pulverization the powders were pressed on opposite sides of a Ni-screen and sintered at 370 °C. It was found that a material of composition $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ shows good catalytic activity and

cycling stability [33]. $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ almost showed no improvement with respect to the pure carbon blank.

Bifunctional air electrodes made using $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ catalyst were operated for more than 400 cycles in electrically rechargeable Zn–air batteries [37]. The surface area of the $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ catalyst material could be optimized by thermal treatment. Well-crystallized materials were found to favor the oxygen reduction, whereas, less crystalline materials are beneficial for oxygen evolution. A material prepared by calcination at 650 °C and subsequent quenching to room temperature showed the most promising performance bifunctional electrodes [38]. The chemical stability of these materials has been investigated by XRD and X-ray spectroscopic methods [39]. The influence of vacuum annealing and subsequent reoxidation on the performance $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_{3-x}$ -type catalysts has been described in [40]. Apparently reoxidation at temperatures as low 200 °C resulted in the maximum activity for oxygen reduction, whereas, the optimum annealing temperature for oxygen generation was found to be 150 °C.

Further work led to catalyst materials of the general composition $\text{La}_{1-x}\text{A}'_x\text{Co}_{1-y}\text{B}'_y\text{O}_3$ ($\text{A}' = \text{Ca}$; $\text{B}' = \text{Mn, Fe, Co, Ni, Cu}$) [34], which were synthesized by the amorphous citrate method [36]. PTFE bonded gas diffusion electrodes were prepared [33] and tested. It can be seen from Fig. 3 that except for the Cu substituted catalyst having significantly lower surface area, all catalysts performed almost identical upon oxygen reduction. However, the Fe substituted material performed best upon oxygen evolution. Cycling experiments using a $\text{La}_{0.6}\text{Ca}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ catalyzed electrode showed

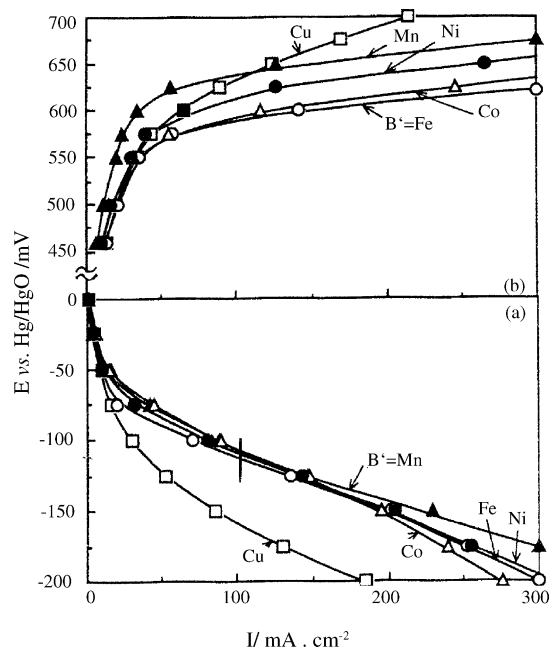


Fig. 3. Polarization curves of gas diffusion electrodes loaded with 25 wt.% $\text{La}_{0.6}\text{Ca}_{0.4}\text{Co}_{0.8}\text{B}'_{0.2}\text{O}_3$ ($\text{B}' = \text{Mn, Fe, Co, Ni, Cu}$) in 7 M KOH at 25 °C (a) cathodic polarization (O_2 reduction) (b) anodic polarization (O_2 evolution) reproduced from [34, Fig. 3].

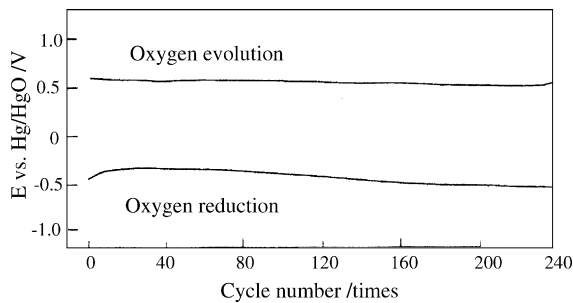


Fig. 4. Test of gas-diffusion electrode loaded with 70 wt.% $\text{La}_{0.6}\text{Ca}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ for the cycles of oxygen reduction (10 min) and evolution (10 min) at 100 mA cm^{-2} (25°C in 7 M KOH) reproduced from [34, Fig. 3].

reasonable stability (Fig. 4). The activity of the materials with respect to oxygen evolution could be correlated linearly with their ability to decompose peroxide (HO_2^-).

As further modifications, catalysts of the general composition $\text{La}_{1-x}\text{A}'_x\text{Fe}_{1-y}\text{B}'_y\text{O}_3$ ($\text{A}' = \text{Sr, Ca, Ba, La}$; $\text{B}' = \text{Mn}$) [35] were prepared by the amorphous mallate method [41] by calcination at 650°C in air. Gas diffusion electrodes having a catalyst loading of 8.1 mg cm^{-2} were prepared [35]. Polarization curves were measured in 7 M KOH at room temperature and H_2O_2 decomposition activity was determined in 9 M KOH at 80°C .

It is evident from Fig. 5 that all catalyst materials show only slight voltage differences in the oxygen reduction reaction. However, oxygen evolution is only sustained when Sr or Ca substituted for the A' position. Sr-substitution showed better performance at oxygen evolution at current densities above 100 mA cm^{-2} , whereas, the Ca substituted material showed slightly better performance upon oxygen reduction.

A strong composition dependence on catalyst performance showing steep maxima was observed for both, A and B-site doping. In the case of Ca substitution, a maximum in anodic and cathodic current was observed at 40% Ca substitution. This maximum correlated with the materials surface area

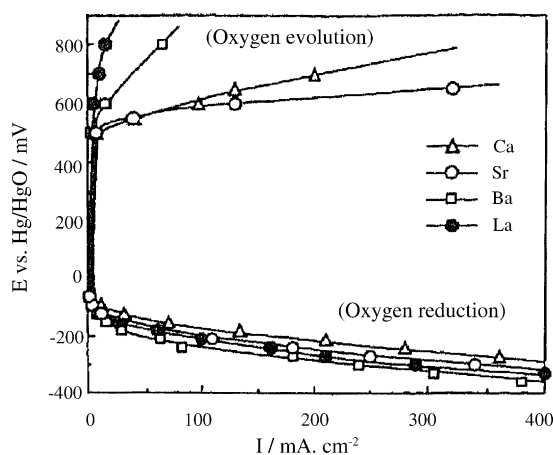


Fig. 5. Cathodic and anodic polarization curves of the oxygen electrodes loaded with $\text{La}_{0.6}\text{A}'_{0.4}\text{Fe}_{0.8}\text{Mn}_{0.2}\text{O}_3$ ($\text{A}' = \text{Ca, Sr, Ba, La}$) in 7 M KOH at 25°C reproduced from [35, Fig. 2].

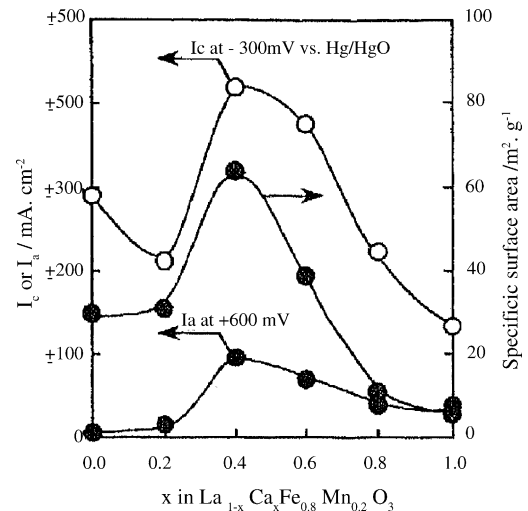


Fig. 6. Cathodic and anodic performances and specific surface area of $\text{La}_{1-x}\text{Ca}_x\text{Fe}_{0.8}\text{Mn}_{0.2}\text{O}_3$ as a function of x reproduced from [35, Fig. 3].

as shown in Fig. 6. The anodic oxygen evolution performance dependence on B-site substitution showed a steep maximum at 20% Mn substitution for Fe (Fig. 7). At higher levels the performance dropped below the one observed for the unsubstituted material. Whereas, the cathodic performance started to form a plateau from 40% substitution of Mn for Fe.

Activity and stability of bifunctional oxygen/air electrodes involving $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ catalysts are also influenced significantly by the carbon used to support the catalyst. This was shown by comparison of electrodes made from high surface area Ketjen black and graphitized Vulcan XC 72. Electrodes made from Ketjen black showed improved performance upon oxygen reduction. However, driving the electrode into oxygen evolution led to a fast deterioration [42].

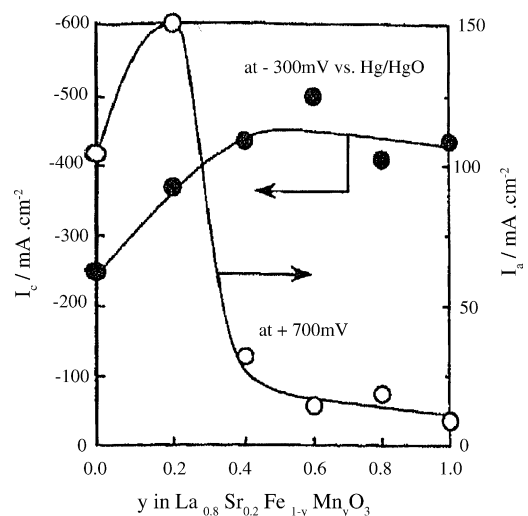


Fig. 7. The current densities of the electrodes loaded with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{1-y}\text{Mn}_y\text{O}_3$ as a function of y (7 M KOH, 25°C , air flow): I_c , cathodic performance (oxygen reduction); I_a , anodic performance (oxygen evolution) reproduced from [35, Fig. 1].

4.2.2. Pyrochlore catalysts

Pyrochlore type oxides have the general formula $A_2B_2O_7$. Their properties can be influenced by the choice of the A and B cations. The properties can be influenced further by doping of the A and B positions. Horowitz et al. [43] were the first to show that oxides with the pyrochlore structure $A_2B_{2-x}A_xO_{7-y}$ (A = Pb/Bi; B = Ru/Ir) were active as bifunctional catalysts in alkaline electrolytes. The application of pyrochlores as catalysts for oxygen electrodes was reviewed by Prakash et al. [44] and Goodenough and Manoharan [45].

A strong dependence of catalytic activity on the composition has been observed. As a bifunctional catalyst the optimum compositions were found to be $Pb_2Ir_2O_{7-y}$ and $PbBiRu_2O_{7-y}$ [46]. However, oxides with the pyrochlore structure show non-negligible solubility in strongly alkaline electrolytes. Stabilization has been achieved by incorporating the catalysts in a polymer electrolyte matrix [45]. Catalysts of composition $Bi_2Ru_2O_7$ showed limited performance for oxygen reduction, however, high activity in peroxide decomposition and improved stability with respect to dissolution under conditions of oxygen evolution.

However, excellent performance for oxygen reduction/evolution has been observed for lead ruthenate pyrochlores when investigated in gas fed electrodes [47]. Substitution of Ir into the materials proved to be beneficial for the oxygen reduction reaction. Furthermore, ruthenium corrosion has been suppressed by covering the catalyst with layers of anion conducting polymers.

Other studies involving Ir oxides some of which had the pyrochlore structure revealed moderate to high activities with respect to the oxygen evolution and lower activity for the oxygen reduction. Materials of composition $Pb_2(Pb_xIr_{2-x})O_{7-\delta}$ and Nd_3IrO_7 showed the highest activities for both reactions [48]. High preparation temperature increased the stability of the materials, whereas, low preparation temperature led to higher activity. Addition of Ta both increased activity and stability.

4.2.3. Spinel catalysts

Besides oxides with the pyrochlore or perovskite structure, metal oxides having the spinel structure are also showing good performance in oxygen evolution and reduction. Oxygen reduction at $NiCo_2O_4$ has been shown with good initial activity however, deterioration is observed with time. Nevertheless, this material is quite stable under the conditions of oxygen evolution [49].

Pure or Li doped cobalt oxide (Co_3O_4) also having the spinel structure is considered a reasonable bifunctional oxygen catalyst [50]. A bifunctional air electrode structure using nickel oxide or spinel type cobalt oxide (Co_3O_4) as an inexpensive transition metal oxide catalyst has been proposed in order to minimize cost and weight of electrically rechargeable Zn–air batteries [51] at the cost of some slight performance sacrifices. The electrode was made from graphite cloth formed from woven graphite fibers coated by graphite powder

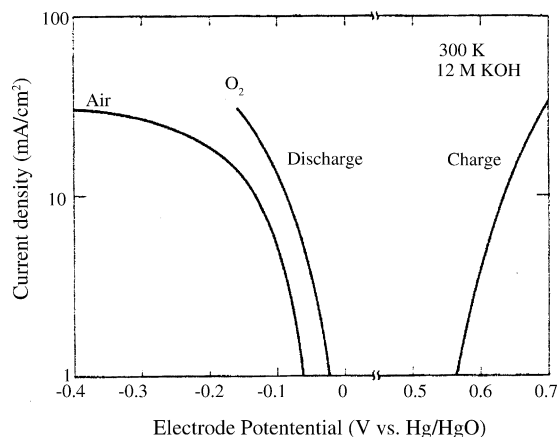


Fig. 8. Polarization curves for a 25 cm² prototype air electrode made entirely from carbon. The electrode was fabricated by impregnating a mixture of graphite and a mixed catalyst made from nickel oxide and spinel type Co_3O_4 into a carbon cloth. The electrode was equipped with a PTFE film-backing layer reproduced from [52, Fig. 6].

of a specific surface area of 25 m² g⁻¹, which was prepared by heat treatment of an inexpensive precursor material. The catalysts were deposited on the graphite according to Ross [52]. The catalyst coated graphite powder was coated on the graphite cloth by teflon bonding and sintering at 350 °C. A second teflon film was roll bonded to the electrode back for wet proofing. Operation at a potential versus Hg/HgO of -130 mV at 10 mA cm⁻² during discharge and +620 mV at 5 mA cm⁻² during charge could be achieved [51]. Electrode start-up under low current density charge for 100 h followed by several conditioning cycles proved to be essential. The high current density performance of the electrode was limited by oxygen transport limitations caused by the PTFE film (Fig. 8). The electrodes were operated in oxygen and in air.

5. Acid electrolytes

Many studies have been published concerning oxygen electrocatalysts in acid media, particularly for use in regenerative fuel cells. Most studies came to the conclusion that Pt/Ir or Pt/IrO₂ in a molar ratio of 1:1. Also mixed oxides from Rh and Ru in a molar ratio of 1:1 or Ir and Rh in a molar ratio of 1–2 were promising electrocatalysts [53–58]. A study using combinatorial chemistry methods was carried out to identify an optimum bifunctional catalyst composition from a combination of Pt, Ir, Rh, Ru and Os [59]. A library of model electrodes of different compositions was prepared by dispersing aqueous solutions of the respective solutions on a teflon coated Toray carbon paper using a plotter. The salts were reduced by sodium borohydride. Electrochemical experiments were carried out at approximately pH 3. The electrodes were simultaneously conditioned by an initial polarization to a potential of 1600 mV (versus RHE) in an electrolyte containing a fluorescence indicator. The oxygen

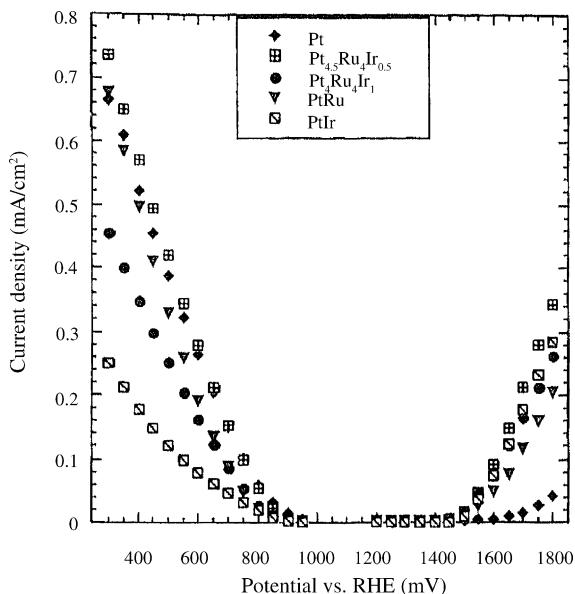


Fig. 9. Polarization curves of bifunctional oxygen electrode in electrolysis (oxygen evolution) and fuel cell (oxygen reduction) modes for different catalysts in 0.5 M H₂SO₄ reproduced from [59, Fig. 4].

evolution activity was measured by stepping the potential from 1200 mV (versus RHE) in steps of 50 mV until visible fluorescence was observed. Oxygen reduction screening was carried out in using a different electrolyte and fluorescence indicator. After conditioning the library at +600 mV (versus RHE), the potential was stepped down from +900 mV (versus RHE) in steps of 50 mV until visible fluorescence was observed. High activity for oxygen reduction and evolution as well as stability towards dissolution was found in rather narrow range of the Pt and Ru rich section of the Pt/Ru/Ir catalyst library. A material with composition Pt_{0.45}Ru₄Ir_{0.5} was found to be particularly active which was also proven by a test of bulk catalyst materials. An activity plot of this material in comparison to other catalysts is shown in Fig. 9. It is evident that the Pt_{0.45}Ru₄Ir_{0.5} material outperforms the commonly used Pt for oxygen reduction and Pt/Ir materials

for oxygen evolution. The material also showed corrosion resistance under the test conditions used.

5.1. Unitized polymer electrolyte membrane fuel cells

A unitized regenerative fuel cell (URFC) is an energy storage system based on hydrogen and oxygen, which can be operated similar to a secondary battery. The system electrolyzes water in charge mode, hydrogen and when appropriate oxygen are subsequently stored. In discharge mode, the system is operated as a fuel cell using up the stored reactants [60]. Significant advantages of the specific energy density can be expected from the use of a URFC (400–1000 Wh kg⁻¹) in comparison to other secondary batteries (220–250 Wh kg⁻¹ for advance Li-polymer batteries). The URFC also offers the advantage of independent sizing of the electrochemical reactor providing power and energy/reactant storage providing the capacity. This advantage is particularly striking in applications where long charge–discharge cycles at a given power are required.

The URFC can be operated in two distinctly different modes as shown in Fig. 10 [61]:

- Oxygen evolution and reduction is taking place at the same electrode, therefore, the use of a true bifunctional electrode is mandatory.
- Anodic reactions such as oxygen evolution upon charge and hydrogen reduction upon discharge take place at one electrode while cathodic reactions such as hydrogen evolution upon charge and oxygen reduction upon discharge are taking place at a different electrode. This method of operation allows catalyst optimization for anodic and cathodic reactions, respectively, which results in considerably lower losses [62]. However, flushing of the electrode compartments with inert gas (e.g. nitrogen) is required when changing from charge to discharge mode.

The most prominent losses are associated with oxygen electrochemistry.

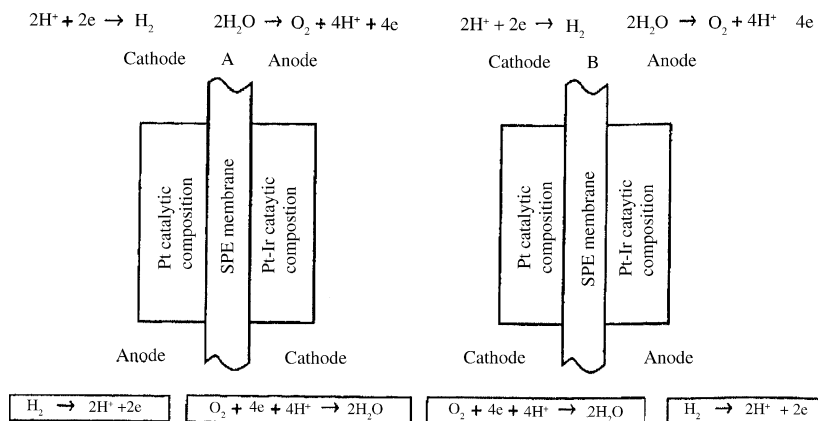


Fig. 10. Modes of operation for a unitized regenerative fuel cell (URFC): (a) oxygen evolution and reduction taking place at the same electrode; (b) anodic and cathodic reactions taking place at the same electrode reproduced from [61, Fig. 1].

5.1.1. Unitized regenerative fuel cells using a single bifunctional oxygen electrodes

Electrodes using internal dual layers have been used in URFC [55]. However, these electrodes are rather bulky and increase the thickness of the gas diffusion path leading to reduced performance.

In order to optimize transport properties, thin layer electrodes were investigated [54]. The electrodes were made by decal transfer method [63] originally developed for high power proton exchange membrane fuel cells (PEFC). In this method, an ink consisting of catalyst powder, ionomer solution (e.g. Nafion in the Na^+ -form) and a high boiling solvent (e.g. glycerol) is spread on a PTFE release blank. After curing the catalyst layer at elevated temperature, it is hot pressed to the electrolyte membrane (e.g. Nafion 115). Afterwards, the PTFE film is removed from the catalyst layer. The membrane electrode assembly (MEA) was rehydrated by boiling in 0.5 M H_2SO_4 . The catalyst loading was 0.4 mg cm^{-2} Pt-black at the hydrogen electrode and 0.4 mg cm^{-2} of a 50:50 mixture of Pt-black and finely dispersed IrO_2 at the oxygen electrode. The thickness of the catalyst layer was about $5 \mu\text{m}$. Carbon paper containing a teflon content of approximately 30 wt.% was used as an electrode backing.

The cell was operated at 80°C at a pressure of 0.3 bar. A current density of 400 mA cm^{-2} at 0.6 V could be achieved in fuel cell mode. In electrolysis mode, 1.71 V were required to obtain a current density of 400 mA cm^{-2} . The cell showed performance improvement within the first cycles (Fig. 11).

Typically, mixtures of Pt and Ir-oxide are used in URFC. An attempt to use supported catalysts has been reported in [64]. Mixed metal catalysts containing Pt, Ir, Ru, Os and Rh were deposited on conductive oxide supports. Ti_4O_7 containing materials as well as $\text{Ti}_{0.9}\text{Nb}_{0.2}\text{O}_2$ have been used as active supports. The highest catalysts stability and activity was found at ternary compositions near $\text{P}_4\text{Ru}_4\text{Ir}_1$ where X-ray near edge spectroscopy showed significant interaction

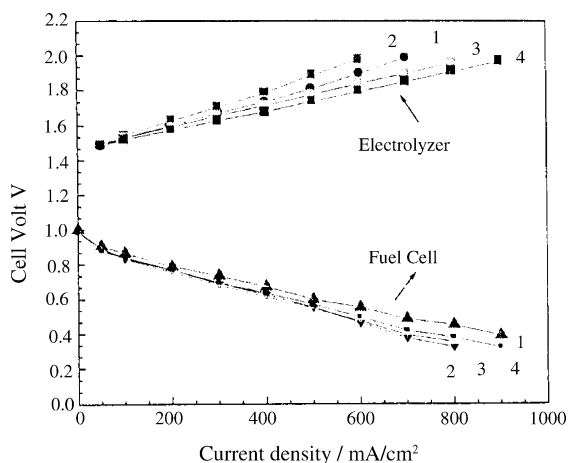


Fig. 11. Performance of a URFC using Nafion 115 electrolyte after four cycles (numbered in the diagram) [54] fuel cell mode: $T=80^\circ\text{C}$, $p_{\text{O}_2}=0.3 \text{ MPa}$, $p_{\text{H}_2}=0.3 \text{ MPa}$; electrolysis mode: $T=80^\circ\text{C}$, ambient pressure reproduced from [54, Fig. 8].

between catalyst and support. The Ti_4O_7 -containing support materials showed significant degradation under oxygen evolution, whereas, $\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_2$ as an oxide with a non-defective oxygen lattice was apparently stable.

5.1.2. Unitized regenerative fuel cells using different electrodes for oxygen evolution/consumption

Work on URFC using different electrodes for oxygen evolution and reduction has been reported in [62]. Different catalysts were studied for both electrodes. Platinum was found to be a reasonably good catalyst for the cathodic reactions i.e. oxygen reduction and hydrogen evolution. A single catalyst for the anodic reactions i.e. hydrogen consumption and oxygen evolution is more difficult to find. Again, hydrogen consumption is best performed at a Pt catalyst. However, oxygen evolution is better performed at an Ir electrode. Since the hydrogen oxidation is a rather reversible reaction even at Ir, a mixture of Pt and Ir is considered a good “oxidation” electrode.

The wetting behavior of the electrodes is of considerable importance for the water management of the cell. In a comparative study [61], it was found that a URFC using different electrodes for oxygen evolution and consumption can possibly be operated with little degradation.

6. Summary

Bifunctional oxygen/air electrodes are still a challenging research topic. In alkaline electrolyte, potentially low cost transition metal oxides are good candidates for bifunctional catalysis. Oxides having the pyrochlore structure containing Ru or Ir show signs of dissolution at elevated potentials even in alkaline electrolytes. Most transition metal oxides, particularly the ones having the spinel structure show higher activity with respect to oxygen evolution. Nevertheless, graphite shows a reasonable activity with respect to two-electron oxygen reduction. Binary oxides such as nickel oxide or spinel type CoO_3 show the highest long-term stability. In connection with transition metal oxides, peroxide reduction is greatly enhanced. In acid electrolytes, the use of noble metals is inevitable.

Unitized regenerative fuel cells having an acid polymer electrolyte can be operated under conservation of anodic and cathodic processes at the same electrodes, respectively, thus reducing losses otherwise seen in more simpler systems where oxygen evolution and consumption takes place at the same electrode. Recent work showed the feasibility of metal oxide supported catalysts for URFCs.

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