

Review



# Mesoporous Nanocast Electrocatalysts for Oxygen Reduction and Oxygen Evolution Reactions

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**Abstract:** Catalyzed oxygen evolution and oxygen reduction reactions (OER and ORR, respectively) are of particular significance in many energy conversion and storage processes. During the last decade, they emerged as potential routes to sustain the ever-growing needs of the future clean energy market. Unfortunately, the state-of-the-art OER and ORR electrocatalysts, which are based on noble metals, are noticeably limited by a generally high activity towards one type of reaction only, high costs and relatively low abundance. Therefore, the development of (bi)functional low-cost non-noble metal or metal-free electrocatalysts is expected to increase the practical energy density and drastically reduce the production costs. Owing to their pore properties and high surface areas, mesoporous materials show high activity towards electrochemical reactions. Among all synthesis methods available for the synthesis of non-noble metal oxides, the hard-templating (or nanocasting) approach is one of the most attractive in terms of achieving variable morphology and porosity of the materials. In this review, we thus focus on the recent advances in the design, synthesis, characterization and efficiency of non-noble metal OER and ORR electrocatalysts obtained via the nanocasting route. Critical aspects of these materials and perspectives for future developments are also discussed.

**Keywords:** oxygen evolution reactions; OER; ORR; nanocasting; mesoporous materials; electrocatalysts; non-noble metals; mixed oxides

## 1. Introduction

Over the last 50 years, our energy needs have almost exclusively relied on the use of fossil fuels or intermittent renewable energy supplies. Unfortunately, the cost and availably of the energy coming from these sources are heavily impacted by various factors such as shortages, geographic and political restrictions, and instability of the market or energy grids. To overcome these issues, intensive research is being conducted on advanced energy storage and conversion systems based on alternative energy sources [1]. The main challenge lies in the development of a safe, efficient and clean way to store energy from renewable and sustainable sources. In addition, with the strong increase in awareness of the general public over environmental concerns, the scientific community as well as industries are pushing forward the introduction of more effective *greener* energy storage devices. Among the various possibilities, technologies based on electrochemical conversions are seen as promising candidates to fulfill these requirements [2].

## 1.1. Oxygen Evolution and Reduction Reactions (OER and ORR)

Many of the "next-generation" energy storage systems such as metal-air batteries (MABs), Zn-air/O<sub>2</sub> batteries (ZABs), reversible fuel cells (RFCs) and water electrolyzers use electrochemical reactions [3–5]. However, despite the fact that the overall performance of these storage systems is directly dependent on the efficiency of the electrochemical reactions taking place at the electrodes during

the charging/discharging processes, they are still not comprehensively explored and/or understood [6–9]. In this way, oxygen-evolving reactions (oxygen evolution/reduction reaction) happening in MABs and water electrolyzers for instance, are of particular interest. Considering the potential economic impact brought by these reactions, the improvement of oxygen evolution (OER) and oxygen reduction (ORR) reactions has become one of the hottest topics in science in recent years [10–12]. In MABs, the ORR takes place during the discharging process whereas the OER takes place during charging [5–7]. Depending on the considered electrolytes, both processes may happen following the equations presented in Scheme 1 [13].

ORR	In acid aqueous system	$\begin{array}{l} O_2 + 4e^- + 4H^+ \to 2H_2O~(4e^-) \\ O_2 + 2H^+ + 2e^- \to H_2O_2~(2+2e^-) \\ H_2O_2 + 2e^- + 2H^+ \to 2H_2O \end{array}$
	In alkaline aqueous system	$\begin{array}{l} O_2 + 4e^- + 2H_2O \rightarrow 4OH^- (4e^-) \\ O_2 + 2e^- + H_2O \rightarrow HO_2^- (2+2e^-) \\ HO_2^- + 2e^- + H_2O \rightarrow 3OH^- \end{array}$
	In an aprotic electrolyte	$O_2 + e^- \rightarrow O_2^-$ $O_2^- + e^- \rightarrow O_2^{2-}$
OER	In acid aqueous system	$2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^-$
	In alkaline aqueous system	$4OH^- \rightarrow O_2 \uparrow +2 H_2 O + 4e^-$
	In an aprotic electrolyte	$O_2^{2-} \rightarrow O_2 \uparrow + 2e^-$

**Scheme 1.** Equations of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in different electrolytes [13].

Briefly, in OER, the production of molecular oxygen relies on several proton/electron-coupled processes [14,15]. Moreover, the reaction is highly pH dependent: In acidic or neutral environments, two water molecules are oxidized into four protons and one oxygen molecule. In basic conditions, hydroxyl groups are oxidized into O<sub>2</sub> and H<sub>2</sub>O [16]. ORR can take place over two pathways—partial or full reduction. Partial reduction involves a two-electron pathway, whereas the full reduction, being more efficient, involves a four-electron pathway. If ORR involves 4 e<sup>-</sup>, higher theoretical energy density can be achieved as compared to the 2  $e^-$  pathway [10,17]. The ORR pathway is not straightforward and depends on the surface properties of the electrode as well as the catalysts used, if any [2]. It involves multiple steps, including oxygen diffusion from the atmosphere to the catalyst surface, oxygen adsorption on the catalyst surface, electron transfer from the anode to the oxygen molecules on the cathode surface to form the discharge product [9,10]. Therefore, for practical applications, a full reduction is preferable in order to reach a higher efficiency. In addition, the reactions involved in OER and ORR are known to be sluggish [18]. It is important to note that to make OER and ORR truly useful for energy storage devices such as MABs, all processes should be reversible to regenerate oxygen molecules during the charging process where OER takes place [9–11,17]. In water electrolysis applications, the main point is to make OER much more efficient since it is the limiting reaction in the overall process, i.e., as compared to hydrogen evolution reactions (HER) [19]. Unfortunately, OER and ORR both suffer from slow kinetics, high overpotential and poor reversibility of oxygen chemistry, significantly limiting the round-trip efficiency when used in metal-air batteries, for example [9–12,17].

#### 1.2. Catalysts for OER and ORR

Improving the activity and stability of ORR and OER can be achieved by using electrocatalysts. Noble metals are highly active catalysts towards oxygen evolving reactions [20]. However, their activity is high only towards one type of reaction, which limits the reversibility, being mandatory for all energy storage applications. For example, platinum-based catalysts are substantially active in ORR but are poor for OER due to the formation of an oxide layer/coating at high potentials [21]. On the opposite side, catalysts containing ruthenium or iridium were shown to be promising for OER only [1,20]. The use of noble metal catalysts is also associated with a tremendous cost increase and subjected to shortage depending on the production and market conditions, ultimately hindering their commercialization [22]. On the other hand, low-cost non-noble metal or metal-free electrocatalysts are expected to increase the practical energy density and reduce the production costs. The development of bifunctional catalysts (active in both ORR and OER) could also bring energy storage devices like reversible MABs closer to the industrial use. As a consequence, the design of high-performance stable catalysts based on compositions/structures such as non-noble (mixed) transition metal oxides, spinels, carbon, and hybrid compositions, is of rapidly growing interest [9-13,17]. Low-cost spinel-type mixed metal oxides (AB<sub>2</sub>O<sub>4</sub>, A = Li, Mn, Zn, Cd, Co, Cu, Ni, Mg, Fe, Ca, Ge, Ba, etc.; B = Al, Cr, Mn, Fe, Co, Ni, Ga, In, Mo, etc.) are particularly promising owing to the possibility of synergy effects between the different metals [13]. For instance, spinel cobaltites have attracted vast attention as bifunctional oxygen electrodes due to their high electrocatalytic activity, and have been tested as catalysts towards ORR/OER [23]. In the same way, (ordered) mesoporous mixed metal oxides and other related mesoporous materials are expected to be highly active towards OER and/or ORR since they show higher activity towards electrochemical reactions as compared to their bulk counterparts, owing to their high specific surface area (often >100  $m^2/g$ ) and their controlled porosity, which not only provide more electrocatalytic sites but also promote mass transport (oxygen and ions) [24]. Among all methods available for the synthesis of mesoporous materials, hard-templating (also called nanocasting or exotemplating) is one of the most attractive in terms of achieving various morphologies and tailored porosity of the materials [25].

#### 1.3. Nanocasting

Nanocasting enables to produce highly ordered non-siliceous mesoporous materials (e.g., metal oxides, carbons, polymers, sulfides, carbides, etc.) with high specific surface area and narrow pore size distribution. It usually requires the use of ordered mesoporous silica, e.g., SBA-15, KIT-6, MCM-48, as a hard template [26]. This technique has several advantages in comparison with other methods, e.g., the widely spread soft templating. Noticeably, the nanocasting approach allows researchers to avoid the necessity to control the hydrolysis-condensation process of inorganic precursors and the cooperative assembly of surfactants and inorganic species. Therefore, it is suitable for a wide range of materials and especially for the preparation of mesostructured mixed metal oxides of various compositions and stoichiometries, which are difficult to prepare via other templating routes [27,28]. This synthesis pathway includes four main steps (Figure 1): (1) the choice and synthesis of the original template (silica, polymers, carbons, etc.); (2) the selection of a suitable precursor salt and its incorporation/confinement (by impregnation, ion-exchange, grafting, etc.) inside the pores of the template; (3) the thermal treatment leading to the decomposition of the sequestered precursor to form the desired oxide; and (4) the selective removal of the parent matrix by chemical etching and/or heat treatment [28].



**Figure 1.** Scheme of the nanocasting synthesis route for ordered mesoporous non-silica materials. Adapted from [29]. Reprinted with permission from The Royal Society of Chemistry.

The choice of the template is driven by two main criteria. First, the template should maintain its ordered mesostructure during the thermal treatment (the third step). Second, the original template should be easily removable without collapse of the mesoporous structure in the resulting replica [26]. For a successful replication, the infiltrated precursor also needs to meet several requirements. The precursor should mostly be passive towards the solid template (silica in the majority of cases), and, to favor diffusion, should also be highly soluble or liquid in standard laboratory conditions. Finally, the conversion to the specific composition should induce a minimum volume shrinkage [26–28]. The infiltration of the precursor into the pore channels is one of the most important steps in the nanocasting method. To do this, there are various techniques depending on the templates and precursors. Wet impregnation [26,28], incipient wetness [26,27], two-solvent method [26], melt infiltration [30,31] and one-step (molten salts) impregnation [32,33] are the most common. In the wet impregnation pathway (or wetness impregnation-calcination method), an excess amount of solvent as compared to the total pore volume of the porous mold is used. The pores are filled due to the migration of the precursor into the pore system via capillary motion happening during the solvent evaporation. While being widely spread and quite simple, this approach has major disadvantages: It is a time-consuming procedure and it leads to a high extent of shrinkage and low level of pore loading (15%–24% depending on the material) [27]. The incipient wetness method, also called dry impregnation, is a synthesis route where a saturated solution of precursors is used, and the pore volume of the original template limits the volume of the solution to be impregnated. The main feature of the method lies in the fact that it usually leads to a higher precursor loading but multiple impregnation steps are often required for optimizing the filling of the pores [26]. One important limitation remains the tedious procedure and the difficulty of scaling up [25–28]. Similar to the incipient wetness, the two-solvent method uses a highly concentrated precursor solution. Here also, the impregnated volume matches the pore volume of the template. An aqueous solution of a precursor is added to the silica template dispersed in dry *n*-hexane. The precursor is then pushed into the pores by the alkane solvent [27]. Finally, the one-step impregnation technique is based on using molten nitrate salts in the presence of an organic solvent (e.g., *n*-hexane, cyclohexane) under refluxing conditions, to infiltrate the mesoporous template. The pores are first filled with alkane solvents, which have much lower surface tension as compared to the highly concentrated salt solutions, prior to being placed in contact with the metal precursors. The high extent of the pore loading, quality of the resulting replicas, low level of shrinkage and conservation of the pore integrity are the main advantages of this approach [25,27]. But for a successful impregnation,

the melting point of the precursors should be lower that of the boiling point of the solvent, which limits the choice of possible precursors.

Overall, while the nanocasting approach is more time consuming in comparison with other synthesis pathways of mesoporous non-siliceous materials, there is still a growing interest for this procedure as evidenced by the amount of scientific research published in the last 10 years on the topic. This flexible synthesis process allows the preparation of composite nanostructures with precisely controlled and easily tuned composition, crystallite and pore size, and pore interconnectivity [23,25]. It results in well-defined nanostructured (mixed) oxides that are of major interest for advanced investigations especially regarding the effect of the materials morphology, porosity and mesostructure on the electrocatalytic performances. For instance, using nanocasting, one may discriminate the role of the parent silica network dimensionality and its consequences on the nanocast, both from a structural and functional point of view, i.e., 2D vs 3D pore structure [34]. In the same way, the effect of the pore size and particle morphology might be systematically rationalized owing to the nanocasting process [35–37]. These latter points are important to understand and require the researchers to establish structure-activity relationships. In this review, the focus will be mainly set on the synthesis and characterization of mixed metal oxides using the nanocasting approach in order to create nanostructured materials that are active in OER or ORR, or both. Experimental data and setups for the electrodes and measurement conditions will be specified to allow a more objective comparison. Few examples based on carbons and other compositions will also be presented. The resulting (nano)porous structural features as well as the behavior of the different materials as electrocatalysts for water splitting (OER only, first part) and for MABs (bifunctional or ORR only, second part) will be examined and summarized. This review emphasizes the importance of the catalyst design, and correlates materials synthesis with the corresponding physico-chemical properties and the efficiency in OER/ORR.

#### 2. Nanocast Electrocatalysts for OER/ORR

#### 2.1. General Aspects

The nanocasting process is a versatile and efficient pathway for the production of (ordered) mesoporous oxidic materials. It usually employs an ordered mesoporous silica as a hard template, followed by the impregnation of metal precursors, thermal formation of the oxide and finally, selective removal of the silica host (see Figure 1). Representative examples of typical N<sub>2</sub> physisorption isotherms, measured at -196 °C, of widely used silica templates, i.e., SBA-15 and KIT-6 hydrothermally aged at 100 °C, and the corresponding nanocast mesoporous (m)Co<sub>3</sub>O<sub>4</sub> are presented in Figure 2. All the parent silica materials exhibit perfect type IV isotherms with well-defined H1 hysteresis loop showing steep capillary condensation and evaporation steps at high relative pressures, being characteristic of high-quality samples with narrow pore size distribution. Nanocast  $mCo_3O_4$  samples also show type IV isotherms with hysteresis loop, confirming the presence of mesopores. However, in contrast to the ordered mesoporous silica hosts, oxide replicas may exhibit different hysteresis loop types with marked features depending on the synthesis process, the chemical composition and the quality of the replica as well as the physico-chemical features of the host materials. The most commonly encountered hysteresis loops for metal oxides are the H3 and H4 ones, which reflect complex pore systems with potential network effects [38]. Typical scanning and transmission electron microscopy images (SEM and TEM, respectively) of mCo<sub>3</sub>O<sub>4</sub> samples nanocasted from KIT-6 and SBA-15 silicas are provided in Figure 3. One can easily see the mesoporous structure of the resulting materials and appreciate the extent of the replication process. In some favorable cases, it is possible to replicate not only the pore system but also the particle shape and size. Nanocast materials made from parent 3D pore structures usually display spheroidal particles (Figure 3a,b) whereas oxide particles obtained from elongated channel-like pore systems will grow in one preferential direction (Figure 3d,e). Such behavior is related to the diffusion of the precursor solution within either a fully 3D interconnected or a unidirectional pore system. Nonetheless, it is important to note that all chemical compositions do not necessary

lead to well-ordered replicas. The influence of the mesopore ordering as well as the physicochemical characteristics of the nanocast oxides on the electrochemical properties of the samples will be discussed in the following sections in more detail.



**Figure 2.** N<sub>2</sub> adsorption-desorption isotherms at -196 °C of KIT-6 silica (**a**), SBA-15 silica (**b**) and the respective nanocast mesoporous Co<sub>3</sub>O<sub>4</sub> replicas (scaled on a second *y*-axis for clarity, on the right).



**Figure 3.** Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of mCo<sub>3</sub>O<sub>4</sub> nanocasts from KIT-6 (**a**, **b**, **c**) and SBA-15 (**d**, **e**, **f**) ordered mesoporous silica materials. Images **a**, **b**, **c** [39] and **d** [34] were reprinted with a permission of © 2014 American Chemical Society.

## 2.2. Application to Water Splitting (OER)

In an early study, Tüysüz et al. [40] synthesized ordered mesoporous (m)Co<sub>3</sub>O<sub>4</sub> from KIT-6 templates aged at different temperatures (35, 100, and 130 °C) via wetness impregnation nanocasting and tested their electrocatalytic activity towards OER at the different pH. The obtained oxides exhibited different specific surface areas (SSAs) (156, 113, and 72 m<sup>2</sup>/g for Co<sub>3</sub>O<sub>4</sub>-35, -100, -130 respectively) and were compared to a bulk Co<sub>3</sub>O<sub>4</sub> with a SSA of 2 m<sup>2</sup>/g. The catalysts were tested using a three electrode standard cell with rotating disk electrode (RDE). The working electrode (WE) was a gold disk electrode (GE) coated with the catalytic ink (loading of 0.13 mg/cm<sup>2</sup>). Pt gauze was used as a counter electrode

(CE) and Ag/AgCl was the reference electrode (RE). Catalytic current measurements were performed in aqueous KOH electrolytes. The current density for ordered mCo<sub>3</sub>O<sub>4</sub> samples was found to increase with increasing specific surface area (27.2 mA/cm<sup>2</sup> was achieved at 1 V (vs Ag/AgCl) for  $Co_3O_4$ -35). Similar results were obtained regarding the oxidative catalytic activity of the  $mCo_3O_4$  as a function of the pH of the electrolyte. Of particular interest, chronoamperometric measurement biased at 0.8 V vs Ag/AgCl at pH = 13 to evaluate the stability of the catalysts showed that the  $Co_3O_4$ -35 sample reached a current density of 8 mA/cm<sup>2</sup> and did not exhibit any deactivation over 100 min. Following this, doping of cobalt oxides by various transition metals has been intensively investigated. For instance, Lu et al. [41] embedded gold nanoparticles (Au NPs, nanoparticles) within mCo<sub>3</sub>O<sub>4</sub>. The use of Au NPs was motivated by the electronegativity of the metal that generates a stronger electronic field for the adsorption of oxygen, making the generation of Co(IV) species easier and ultimately increasing the overall activity of the Au/Co catalyst [42,43]. Among all materials, 2.5 wt % Au/mCo<sub>3</sub>O<sub>4</sub> revealed a highly ordered structure with a narrow pore size distribution, high SSA (109 m<sup>2</sup>/g) and uniformly distributed Au NPs within the  $mCo_3O_4$ . The catalytic performance of this material was then tested with the 3-electrode standard system with Ag/AgCl in 3M KCl as a reference electrode, and modified glassy-carbon RDE as a working electrode. The polarization curves confirmed the improved catalytic activity of the Au-doped cobalt oxide as compared to pure mCo<sub>3</sub>O<sub>4</sub>. Moreover, the composite demonstrated an excellent stability during 2000 cycles. Remarkably, the calculated turnover frequency of Au/mCo<sub>3</sub>O<sub>4</sub> (0.048 s<sup>-1</sup>) was much higher than that found for mCo<sub>3</sub>O<sub>4</sub> (0.026 s<sup>-1</sup>) and other data reported so far.

Increasing the amount of Au NPs was not beneficial since it led to a lower SSA resulting in lower number of reactive catalytic sites and therefore, a decrease in the activity towards OER. Thus, it was rapidly identified that high SSA in the mesoporous replicas was highly desirable for electrocatalytic activity. Following similar reasoning, a complementary work used palladium nanoparticles (Pd NPs) which were dispersed onto  $mCo_3O_4$  [44]. Pd has a much higher conductivity and has shown a substantially higher catalytic activity for OER as compared to gold. High amount of Co(IV) species were obtained by dispersion of Pd NPs onto a 3D nanostructured Co<sub>3</sub>O<sub>4</sub> material obtained via nanocasting of KIT-6 silica. The resulting Pd/Co<sub>3</sub>O<sub>4</sub> sample had a SSA of 81  $m^2/g$  and a relatively small mode pore size of 1.1 nm. However, this value was obtained using the Barrett-Joyner-Halenda (BJH) method, which is known to severely underestimate the pore size of materials, especially below 10 nm [45]. In the same way, the reported pore volume (0.03 cm<sup>3</sup>/g) does not seem to be in agreement with the presented physisorption data. Nevertheless, the Pd-modified sample (1:1 wt ratio) demonstrated an enhanced activity towards oxygen evolution by 1.6 times compared to mCo<sub>3</sub>O<sub>4</sub>, thanks to synergistic effects between the two metals [46]. Interestingly, the lowest onset potential and the highest current density were obtained for a sample containing half less Pd (50 wt % of Pd), highlighting the importance of such bimetallic systems. One may aim for a high surface over volume ratio in order to maximize the activity of the dopant. Furthermore, long-term chronoamperometry measurements showed an excellent durability in comparison to the pristine  $mCo_3O_4$ . All electrochemical measurements discussed above were carried out with a standard three-electrode cell using 0.1 M KOH solution as an electrolyte, a graphite rod as a working electrode, a platinum foil  $(3.0 \text{ cm}^2)$  as a counter electrode, and a saturated calomel electrode (SCE) with a salt bridge as a reference electrode.

Another example of "doped" cobalt oxides was reported by Grewe et al. [39]. However, in this study, instead of noble metals, a non-noble transition metal, i.e., Fe, was added. Fe-mCo<sub>3</sub>O<sub>4</sub> oxides were prepared via a wetness impregnation protocol using a standard KIT-6 as the template and a solution of cobalt and iron precursors in different ratios. The extent of the pore ordering in the nanocast replicas was found to be inversely correlated with the Fe/Co ratios, i.e., higher ratios led to less ordered structures. All the doped samples had a similar SSA around 120 m<sup>2</sup>/g, and a total pore volume in the range of 0.3–0.4 cm<sup>3</sup>/g. For the electrocatalytic characterization, a three-electrode cell with Ag/AgCl was used as the reference electrode, Pt wire as the counter electrode, and aqueous KOH solution was chosen as the electrolyte. The working electrodes were fabricated by deposition of the catalytic ink on

glassy carbon (GC) electrodes. The catalytic activities towards OER of pure  $mCo_3O_4$  and Fe-doped ones are presented in Figure 4.



**Figure 4.** Oxygen evolution currents of  $Co_3O_4$  and Fe- $Co_3O_4$  with various Co/Fe atomic ratios (64, 32, 16, 7, 3, and 1) [39]. Reprinted with a permission of © 2014 American Chemical Society.

Fe-mCo<sub>3</sub>O<sub>4</sub> samples with ratios Co/Fe = 32 and Co/Fe = 64 had the highest catalytic activity and high current density at 1 V (vs Ag/AgCl): 33.8 mA/cm<sup>2</sup> and 31.3 mA/cm<sup>2</sup>, respectively. However, the introduction of large amounts of iron (atomic ratio > 0.1) led to the co-formation of CoFe<sub>2</sub>O<sub>4</sub> inverse spinel, which resulted in lower catalytic activities. It was thus suggested that fine distribution of Fe atoms within the  $Co_3O_4$  crystal structure was preferential for enhanced catalytic activities, in good agreement with the results obtained for Pd-mCo<sub>3</sub>O<sub>4</sub> discussed above. This effect was attributed to a change in electronic structure of the material that might affect the conductivity and charge transfer properties. Accurate control of the dopant metal is thus mandatory for the successful synthesis of a potent electrocatalyst. However, since each metal may present a different behavior and affect the final catalyst pore structure in various ways, it appears difficult to predict the optimal loading and a trial and error approach might unfortunately be applied to find the best composition. In this way, Xiao et al. [47] also incorporated Fe and/or Ni into the structure of mesoporous  $Co_3O_4$ . Similar to Grewe et al. [39], the catalysts were prepared via wetness impregnation nanocasting using KIT-6 silica as the template. In line with the literature, high-quality replicas of mesoporous cobalt oxide with a cubic pore symmetry were obtained. Further, the effect of the dopant nature onto the pore structure was rationalized. The addition of 10 wt % of Ni into  $mCo_3O_4$  did not significantly change the porous architecture whereas addition of Fe (10 wt %) or Fe-Ni (5 wt %–5 wt %) led to the formation of slit-like pores of broad pore size distribution, as suggested by nitrogen physisorption experiments. Electrocatalytic activity of the resulting oxides was tested using a standard three-electrode cell, a catalyst-loaded glassy carbon working electrode, an Ag/AgCl (3 M KCl) reference electrode and a Pt wire counter electrode. Among all the synthesized catalysts, Fe-mCo<sub>3</sub>O<sub>4</sub> demonstrated the highest OER activity, which was also higher than the activity of the Au-mCo<sub>3</sub>O<sub>4</sub> system described above [41]. The enhanced activity was attributed to the synergistic effect between Fe and Co, the changes of the mesoporous structure related with the introduction of Fe and to the increased conductivity as compared to the pristine mCo<sub>3</sub>O<sub>4</sub>. Unfortunately, no low angle X-ray diffraction (XRD) experiments were performed to further investigate the extent of modifications in the pore structure and ordering, making it hard to conclude on

the importance of the pore shape, network structure and pore ordering. The synergistic effect between Fe and Co was indirectly substantiated by the results obtained on Ni-mCo<sub>3</sub>O<sub>4</sub> and NiFe-mCo<sub>3</sub>O<sub>4</sub>. Both materials showed similar lower catalytic activity. Therefore, it was proposed by the authors that the sites occupied by some Ni in the crystal structure suppressed the synergistic effects between Fe and Co. Durability tests demonstrated that the Fe-mCo<sub>3</sub>O<sub>4</sub> catalyst retained excellent stability and activity over 450 cycles. Mesoporous oxides nanocasted from KIT-6 silica with variable Co/Ni ratios were further reported by Deng et al. [48]. The materials had Brunauer–Emmett–Teller (BET) SSAs in the range of 90–110 m<sup>2</sup>/g and pore volumes around 0.35 cm<sup>3</sup>/g, which is rather typical for the replicas templated from KIT-6 aged at 100 °C [40,47]. Moreover, all samples had a narrow pore size distribution centered at around 3 nm. The electrochemical tests were performed in standard three-electrode system using a modified glassy carbon RDE as a working electrode, reversible hydrogen electrode (RHE) as a reference, and Pt wire as a counter electrode. The importance of this work lies in the study of the electrochemical "activation" of Ni-containing oxides, and how the purity of the KOH electrolyte influences the catalytic activity. Indeed, several groups [49,50] previously reported that nickel-based oxides/hydroxides could be converted to oxyhydroxide species resulting in a more efficient water oxidation reaction. Higher activity can thus be achieved through an activation procedure. Results published by Deng and co-workers validated this observation [48]. Linear scanning voltammetry (LSV) polarization curves were collected before each cycle of 50 cyclic voltammetry (CV) runs, ultimately aiming to obtain an invariant LSV curve. The total number of CV runs performed was dependent on the catalyst composition. Still, the activation process was found to shift the overpotential to lower values and increased the catalytic activity for all Ni-containing oxides. The effect was even more pronounced for doped spinel-form oxides while deactivation after the long-term tests was observed for pure  $mCo_3O_4$ . The most active sample had a Co/Ni ratio of 4 and exhibited an overpotential  $\eta \approx 336$  mV after the activation step, which is among the lowest values reported, to the best of our knowledge, for Ni-Co based oxides tested for OER. Of particular importance, this activation led to a far superior mass activity ( $\approx$  8 times higher as compared to a non-activated sample) and current densities, being stable for 14 h. No changes in the mesoporous ordering and crystallinity were noted after the electrochemical measurements, confirming the appreciable stability of the material. Furthermore, impedance spectroscopy demonstrated that the transfer resistance of this electrocatalyst was almost divided by 5 times after activation, which indicates a significant enhancement of oxygen evolution kinetics. For comparison purposes, a sample with the same composition (Co/Ni = 4) was also synthesized using a silica gel as a template. The activation process had a similar effect on the disordered mesoporous oxide, confirming that the activation process is related to the crystal structure and not dependent on the mesoporous ordering of the material. However, nickel cobalt oxide with an ordered mesoporous structure still exhibited higher activity as compared to the disordered one, highlighting again the impact and the importance of an ordered/easily accessible pore structure, e.g., 3D pore network. The synthesis of mesoporous mixed transition metal oxides based on Ni and Fe (NiFe<sub>2</sub>O<sub>4</sub>, NFO) was also reported by the group of Du [51]. The authors used a defect engineering strategy to increase the electrocatalytic activity towards OER. All electrochemical measurements were performed in a standard three-electrode system where saturated Ag/AgCl and platinum wires were used as a reference and counter electrodes, respectively. A modified glassy carbon RDE was used as the working electrode. Catalysts were prepared by a one-step impregnation nanocasting method using SBA-15 as a template combined with a reduction under gas at different temperatures [51]. As expected, higher reduction temperatures led to mesoporous oxides with lower SSA (from 261 m<sup>2</sup>/g to 165 m<sup>2</sup>/g). One of the most interesting point of this study was the in-depth investigation of the mesoporous oxide structures with extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) analyses that clearly revealed the existence of oxygen vacancies in the samples reduced at high temperatures, i.e., 280, 300, and 320 °C (NFO-280, -300, -320). In addition, using X-ray photoelectron spectroscopy (XPS), oxygen species were shown to preferentially chemisorb at the surface of the NFO defect centers. These results were directly correlated with the electrocatalysis behavior of

the materials since all the defective NFO catalysts exhibited higher activity towards OER, i.e., smaller overpotentials and onset potentials, as compared to the defect-free sample (NFO-0). The mesoporous oxide NFO-320 exhibited the highest specific mass and area activities at an overpotential of 0.35 V, i.e., 17.5 A/g and 0.106 A/m<sup>2</sup>, being  $\approx$  23 times and  $\approx$  36 times higher than the values obtained for NFO-0, respectively. Defective NFO-320 showed an excellent durability for 40 h combined with a conservation of its lattice structure and a good stability over time. Thus, it can be concluded that defect engineering is desirable as it leads to increased amount of the active sites and higher conductivities, ultimately enhancing the catalytic activity towards OER. Moreover, considering that these NFO samples were replicated from a 2D silica template, i.e., SBA-15, and the results described earlier in this paragraph, it would be interesting to apply this approach for NFO materials made from a 3D mold structure.

In addition to transition (bimetallic) oxides, transition metal phosphides have also been investigated as highly affective catalysts towards OER [52]. The first synthesis of a family of bimetallic Co-Ni phosphides (CoNiP) was done in 2016 by Fu et al. [53]. Samples were nanocasted via a wetness impregnation procedure from KIT-6 silica and all exhibited ordered mesoporous structures with a pore size around 8 nm regardless of the stoichiometry (Co<sub>3</sub>NiP, CoNi<sub>3</sub>P, CoNiP), demonstrating the versatility of the nanocasting process. All electrochemical measurements were performed in a standard three-electrode system using a Pt foil and a saturated calomel electrode (SCE) as the counter electrode and the reference electrode, respectively and a coated glassy carbon RDE as a working electrode. Studies of single metal phosphides had shown that CoP exhibited even better activity than commercial RuO<sub>2</sub>, which is considered to be the reference catalyst for OER [54]. To probe the effect of the chemical composition, bimetallic samples with different Co/Ni ratios were investigated in the same way as single metal phosphides. The sample prepared using precursors with a molar ratio of Co/Ni = 3 had the lowest onset potential among all the obtained samples and  $RuO_2$ , as well as the highest activity for OER (225.5 mA/cm<sup>2</sup> at 1.65 V). The kinetics, evaluated from the Tafel slope, were also found to be better for the Co<sub>3</sub>NiP catalyst as compared to the commercial RuO<sub>2</sub>. Moreover, the sample showed excellent stability during 12 h. Overall, the use of bimetallic phosphides catalysts allowed a 60% current enhancement while conventional  $RuO_2$  showed a 37% loss on the current density. The authors proposed that the superior catalytic activity of  $Co_3NiP$  was related to the lower reaction-free energy caused by the introduction of bimetallic phosphides and a properly tuned composition.

As discussed above, the hard-templating approach appears to be an efficient and flexible method to synthesize functional mesoporous electrocatalysts based on transition metals, with narrow pore size distribution and high SSA. However, one of the main drawbacks of this method is the low amount of produced materials. Therefore, it is mandatory to scale up the process to truly evaluate its potential and limitations. In this way, Deng et al. [55] presented a method to use spent tea leaves (STL) for the preparation of cobalt-based mixed oxide nanocrystals as catalysts for OER. Doped (Cu, Ni, Fe, and Mn, M/Co = 1/8) nanocast mCo<sub>3</sub>O<sub>4</sub> were synthesized in a larger amount, i.e., 8 g, using a wet impregnation technique. XRD analyses showed that the obtained materials had spinel structures with different lattice parameters depending on the doping metal used. The calculated BET SSAs were all in the range of  $34-63 \text{ m}^2/g$ , in good correlation with the crystal size calculated from powder XRD. It is important to note that the materials obtained from the scaled-up synthesis protocol exhibited similar textural and structural characteristics as compared to the samples obtained using the "usual small scale" process. This approach was also shown to be versatile as the authors were able to synthesize relatively high amounts of mCo-based oxides starting from five different types of tea leaves. Electrocatalytic activity was tested in a standard three-electrode system with coated glassy carbon (GC) RDE, RHE and Pt wire as a working, reference, and counter electrodes, respectively. At the exception of the Mn doped sample, Ni-, Cu-, and Fe-mCo oxides demonstrated enhanced catalytic activity, i.e., lower overpotential of 10 mA/cm<sup>2</sup> and improved kinetics according to the Tafel slope, in comparison to pristine mesoporous and bulk Co<sub>3</sub>O<sub>4</sub> oxides. mCo oxides synthesized from different tea leaves exhibited an enhanced activity as well, and samples with higher BET SSA showed increased activity, in good agreement with previously reported results [40,56]. Although the presented electrocatalytic results were promising, the most appealing aspect of this work still remains the possibility to use the nanocasting method to synthesize catalytic materials (for fuel cells) in larger amounts. Yu et al. later extended their work to Ni/Fe-based oxides for OER [57]. Variable Ni/Fe ratios were investigated in order to find an optimal composition regarding the electrocatalytic activity. The optimal catalyst (Ni/Fe = 32/1) performed with a high activity (current density after activation is 32.4 mA/cm<sup>2</sup> at 1.7 V vs RHE), a small reaction resistance, large exposed electrochemical surface area (ECSA) and a superior intrinsic activity due to the introduction of Fe. Aiming to demonstrate the industrial applicability of their process, the authors fabricated a catalyst-coated nickel foam electrode, which exhibited large current density, and an activity maintained over 2 days. Finally, these two additional reports confirmed the essential role of the stoichiometry in the electrocatalytic activity of the mixed metal oxides. Here also, the trial and error/screening approach appeared as mandatory to investigate the different metals and isolate the best composition. One may keep in mind that such experiment design is unfortunately quite time and resource consuming. Also, since it may be metal-dependent, it is difficult to draw clear conclusions regarding the role of the pore structure ordering as well as the optimal pore size or pore size range for the application in OER.

#### 2.3. Prospects for Applications in Metal-Air/Ion Batteries (Bifunctional; Only ORR)

Bifunctional catalysts are interesting for metal-air/oxygen batteries since they might reduce the production costs and simplify the manufacturing process. During the last years, various studies were reported regarding the use of single or mixed metal oxides for both OER and ORR. For instance, Sa et al. [56] prepared two mCo<sub>3</sub>O<sub>4</sub> using wetness impregnation nanocasting and KIT-6 silica aged at different temperatures, i.e., 35 and 100 °C, as templates. The BET SSAs for the mCo<sub>3</sub>O<sub>4</sub>-based samples were 114 m<sup>2</sup>/g and 135 m<sup>2</sup>/g, for materials aged at 100 and 35 °C, respectively. The resulting electrocatalytic activity of the nanocast  $mCo_3O_4$  was then compared to the one of  $Co_3O_4$  nanoparticles synthesized via a hydrothermal method and with Ir loaded (20 wt %, incipient wetness) Ketjen black carbon. A three-electrode cell with glassy-carbon RDE coated with catalytic ink was used as a working electrode, Hg/HgO as a reference electrode, and Pt-wire as a counter electrode. The catalyst loading on the WE was set at 0.1 mg/cm<sup>2</sup>. The OER activities of the catalysts were measured using a RDE in a 0.1 M KOH electrolyte solution with LSV from 1.0 to 1.7 V (vs RHE) at a scan rate of 5 mV/s. As shown in Figure 5, mCo<sub>3</sub>O<sub>4</sub> was more active towards OER as compared to bulk and Co<sub>3</sub>O<sub>4</sub> NPs as well as Pt/C. It also showed current densities close to those obtained with Ir/C. Moreover, the activity was enhanced with the mesoporous samples exhibiting higher specific surface areas, which correlates well with the results of Tüysüz and coworkers [40]. Interestingly, the two mCo<sub>3</sub>O<sub>4</sub> catalysts showed nearly identical polarization curves for ORR, i.e., the onset and half-wave potentials values were around 0.75 V and 0.62 V, respectively, and curves had well-defined plateaus corresponding to diffusion-limiting current at around  $5.5 \text{ mA/cm}^2$ . These results clearly indicate that the mesoporous cobalt oxides had good catalytic activities towards both ORR and OER, ultimately improving the kinetics of these reactions. Regarding the catalyst stability, the OER activity (at 1.65 V) of mCo<sub>3</sub>O<sub>4</sub>-35, i.e., the sample nanocasted from a KIT-6 aged at 35 °C, showed a 29% loss of activity only after 1500 CV cycles while Co<sub>3</sub>O<sub>4</sub> NPs showed a much more severe degradation, i.e., an activity loss of 41%. This result was postulated to be related with the 3D interconnected pore structure of  $mCo_3O_4$ -35 that may improve the durability via a better retention of the original structure after the cycling. Unfortunately, it was not really possible to conclude on the effect of the pore size of the starting template since the mCo<sub>3</sub>O<sub>4</sub>-100 material was not fully compared to its analogue synthesized at 35 °C. However, since mCo<sub>3</sub>O<sub>4</sub>-35 exhibited a higher SSA, it may explain its superior electrocatalytic and durability behavior. In a similar study, using MnO<sub>2</sub> this time, Selvakumar et al. [58] synthesized 2D and 3D mesoporous oxides from a variety of different templates, i.e., MCM-41, SBA-15, MCM-48 and KIT-6. The resulting ordered mesoporous samples had moderate SSAs (28–50  $m^2/g$ ) and pore volumes in the range of 0.1–0.8  $cm^3/g$ , with the highest values obtained for the replica of the KIT-6 silica. Moreover, it was demonstrated that the replication process was more successful for materials exhibiting larger mesopores, i.e., SBA-15 and

KIT-6. All electrochemical tests were performed in a standard three-electrode system with R(R)DE as a working electrode, Ag/AgCl as a reference electrode, and Pt wire as a counter electrode. Among all the samples, 3D mMnO<sub>2</sub> showed enhanced catalytic activity towards both OER and ORR in comparison to bulk and nanocast materials based on a 2D template. These results, being in line with the observations discussed above, may be explained by the enhanced electronic mobility and favored mass transport of charges in 3D materials compared to their 2D analogues. The stability tests performed on 3D materials also revealed a better durability (8000 s) for MnO<sub>2</sub>-KIT-6 as compared to MnO<sub>2</sub>-MCM-48 (less than 5000 s). The durability of  $MnO_2$ -KIT-6 was comparable to the one of commercial IrO<sub>2</sub>. Overall, 3D ordered mesoporous manganese oxide, nanocasted from "large pores" silica showed excellent and promising bifunctional performances towards ORR and OER. However, it is difficult to conclude on the effect of the pore size from this study, except for the ease of replication, since the mesoporous oxides nanocasted from MCM-48, MCM-41 and KIT-6 silicas all exhibited a similar pore size of 6.2 nm, whereas the one made from SBA-15 had bigger pores, i.e., about 9 nm. It remains that replicas made from large pore silica, SBA-15 and KIT-6, resulted in materials with larger pore volumes. Therefore, according to the results presented by the authors, the optimal combination for efficient nanocasting seems to be the use of a 3D silica template having sufficiently large mesopores and pore volume, typically, KIT-6 and related materials.



**Figure 5.** OER polarization curves for meso-Co<sub>3</sub>O<sub>4</sub>-100, meso-Co<sub>3</sub>O<sub>4</sub>-35, Co<sub>3</sub>O<sub>4</sub> NPs, commercial Co<sub>3</sub>O<sub>4</sub>, Ir/C, and Pt/C catalysts [56]. Reprinted with permission from The Royal Society of Chemistry.

In comparison to other metal oxides, cobalt oxides have still drawn the most promises because of their reasonably high catalytic activity, ease of preparation and good chemical stability. However, cobalt is potentially toxic and is relatively costly. Combined with the fact that cobalt is now included in the list of critical raw materials [59], there is a strong interest to at least partially replace some Co in  $Co_3O_4$ -based materials by cheaper and more ecofriendly metals. In this direction, Li et al. [60] reported the synthesis of 3D ordered mZnCo<sub>2</sub>O<sub>4</sub> (3DOM (three-dimensional ordered mesoporous) ZnCo<sub>2</sub>O<sub>4</sub>) via a wetness impregnation approach, using KIT-6 silica as a template and Zn and Co nitrates as precursors. The obtained material had a relatively high BET SSA of 127 m<sup>2</sup>/g with a narrow pore size distribution, centered at 3.4 nm. In contrast to most studies reported in the literature, the resulting catalysts were incorporated in Li-O<sub>2</sub> coin batteries (2025 type) in order to perform advanced and more realistic electrochemical tests. The oxygen cathodes were prepared by coating a current collector with the homogenous catalytic ink (1.1 mg/cm<sup>2</sup> loading). An aprotic electrolyte, i.e., 1 M LiCF<sub>3</sub>SO<sub>3</sub> in tetraethyleneglycoldimethylether (TEGDME), was used and the discharge/charge tests were carried out under an oxygen atmosphere. Specific capacities of 6024, 3710, 3119, and 1674 mA·h/g were obtained for Li-oxygen batteries containing 3DOM ZnCo<sub>2</sub>O<sub>4</sub> at 100, 200, 500, and 1000 mA/g, respectively. These values are much higher than the ones reached with pure carbon at all investigated current densities. In addition, it was observed that the  $ZnCo_2O_4$  cathode could be discharged and charged stably for at least 27 cycles above 2.0 V, whereas the carbon electrode was stable only during 7 cycles (at 100 mA/g under a specific capacity limit of 500 mAh/g). Here also, these encouraging results were thought to be related with the enhanced catalytic activity of spinel-type ZnCo<sub>2</sub>O<sub>4</sub> and its 3DOM large pore structure. Furthermore, XPS analyses showed the apparent reversible formation and decomposition of Li<sub>2</sub>O<sub>2</sub> during charge and discharge cycles onto the carbon electrode. SEM observations further confirmed some differences between the electrode surface before and after the discharge process. From these data, the authors concluded that the process of formation and decomposition of Li<sub>2</sub>O<sub>2</sub> was reversible. Following this, a more promising composition, i.e., spinel  $CuCo_2O_4$ , was proposed by the same group [61]. The electrocatalytic tests were conducted on a battery constituted of an oxygen cathode (a current collector coated with the catalytic ink), a glass filter separator, a non-carbonate electrolyte containing 1M LiCF<sub>3</sub>SO<sub>3</sub> in TEGDME and a metallic lithium foil anode. The CuCo<sub>2</sub>O<sub>4</sub>/carbon electrode exhibited a higher cathodic peak voltage, a lower anodic onset potential, and much larger cathodic and anodic currents in comparison to the pure carbon electrode. More importantly, the specific capacity for the  $Li-O_2$  battery with  $CuCo_2O_4$  electrode was again much higher than the one observed for the pure carbon electrode, i.e., 7456, 3606, and 2692 mA·h/g at 100, 200, and 500 mA/g, respectively. An energy density of 1350 W·h/kg (500 mA·h/g  $\times$  2.7 V) could be achieved, which is about twice the energy density of commercial cathodes in Li-ion batteries (640 W·h/kg, 160  $mA \cdot h/g \times 4 V$ ).

Oxides based on both cobalt and nickel were applied as highly active catalysts towards OER. In 2014, Li et al. [62] synthesized a 3DOM NiCo<sub>2</sub>O<sub>4</sub> from a KIT-6 template using the wetness impregnation technique. The obtained material, exhibiting a specific surface area of 95  $m^2/g$  and bimodal mesopores of about 3.5–5.0 and 7.5–8.0 nm, was then tested as a bifunctional catalyst towards both ORR and OER (with inks containing variable oxide wt %). A swagelok cell with an air hole of 10 mm diameter was used. The electrolyte was made out of 1 M LiCF<sub>3</sub>SO<sub>3</sub> in TEGDME. A metallic Li foil with a thickness of 0.50 mm was used as the anode, and a carbon paper coated with the catalytic ink was used as the cathode. Higher current densities, higher ORR and lower OER onset potentials were obtained for most 3DOM NiCo<sub>2</sub>O<sub>4</sub>/carbon electrodes as compared to the classical carbon one. The electrodes with 0 wt% (pure carbon), 20 wt %, 45 wt % and 70 wt % mNiCo<sub>2</sub>O<sub>4</sub> showed specific capacity of 3993, 4357, 4120 and 1881 mA·h/g, respectively. Moreover, the addition of mNiCo<sub>2</sub>O<sub>4</sub> increased the round-trip capacity efficiency of Li-O<sub>2</sub> batteries from 23.2% (for the pure carbon) to 78% (for the mixture). The optimal ink, containing 20% mNiCo<sub>2</sub>O<sub>4</sub>, not only provided the best specific capacity, but also a promising capacity retention rate after 5 cycles, i.e., 41.9%. Ren et al. reported similar research on ordered mNiCoMnO<sub>4</sub> [63] synthesized via the wetness impregnation method and NiMn<sub>2</sub>O<sub>x</sub> [64] synthesized via the two-solvent method, using KIT-6 as a hard template in both cases. The authors expanded on the synthesis conditions and explored the effect of the annealing temperature (200, 550, 700, and 800 °C for NiCoMnO<sub>4</sub> and 600 and 800 °C for NiMn<sub>2</sub>O<sub>x</sub>) on the properties of the metal oxides. Most of the resulting catalysts exhibited SSAs in the range of  $100-150 \text{ m}^2/\text{g}$  and pore volumes between 0.21 and 0.26 cm<sup>3</sup>. One particular material, NiMn<sub>2</sub>O<sub>x</sub>-600, showed a rather large pore volume of 0.48 cm<sup>3</sup>/g (with a BET SSA of 143 m<sup>2</sup>/g). When compared to its analogue annealed at 800 °C in CV, Ni $Mn_2O_x$ -600 reached much higher current densities (Figure 6a,b). Moreover, the capacitance of NiCoMnO<sub>4</sub>-800 at 1 mV/s was about 2/3 of the value of NiMn<sub>2</sub>O<sub>x</sub>-600, i.e., 90 F/g. These data were recorded using a three-electrode cell at room temperature. The catalytic inks were pressed onto nickel foam current-collectors to make the electrodes (mass loading 1.0 mg/cm<sup>2</sup>). A mixture of 0.1 mol/L Na<sub>2</sub>SO<sub>4</sub> was used as the electrolyte. Platinum foil and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Here, it is interesting to discuss the role of specific surface area. Indeed, when the capacitance values are normalized vs. the specific surface area, the two materials have almost the same capacitance, i.e., 0.67 F/m<sup>2</sup> for NiCoMnO<sub>4</sub>-800 and 0.63 F/m<sup>2</sup> for NiMn<sub>2</sub>O<sub>x</sub>-600. Therefore, being able to produce stable and durable ordered mesoporous catalysts with high SSA and

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3D porosity appears as a key objective to reach optimal efficiency in both OER and ORR. To further investigate the effect of porosity, Li et al. [65] synthesized four KIT-6-like templates with different acid concentrations, i.e., 0.5–1.5 M HCl, and different aging temperatures, i.e., 40–130 °C. The NiFe<sub>2</sub>O<sub>4</sub> nanocasts obtained from these templates were mixed in a catalytic ink and then coated on a carbon paper (loading of  $1.0-1.2 \text{ mg/cm}^2$ ). 1M LiCF<sub>3</sub>SO<sub>3</sub>-TEGDME was used as an electrolyte. LSV was conducted in a three-electrode electrochemical cell with the previously mentioned oxygen electrode as the working electrode and lithium metal foils as the counter and reference electrodes. Again, all 3DOM NiFe<sub>2</sub>O<sub>4</sub>/carbon electrodes exhibited higher activity towards both ORR and OER as compared to the standard carbon electrode. Interestingly, the activity of 3D ordered mNiFe<sub>2</sub>O<sub>4</sub> gradually increased as a function of the pore size and pore volume. The specific capacities of Li-O2 batteries with 3DOM NiFe<sub>2</sub>O<sub>4</sub> catalysts were all above 10,000 mA $\cdot$ h/g<sub>C</sub>, which is much higher than the value obtained for the standard carbon electrode, i.e., 4454 mA·h/g<sub>C</sub>. The best catalyst was found to be that with the largest pore size and pore volume but exhibiting the least ordered structure. All BET SSAs were in the range of 90–123 m<sup>2</sup>/g. From this work, it thus appears that a high SSA only is not sufficient for a catalyst to be efficient. Clearly, the role of the pore structure, i.e., 3D vs. 2D, and its mode pore size are also important parameters that cannot be overlooked. The impact of mesostructured ordering is however still unclear. Yet, from the current state-of-the-art, it seems that the most promising catalysts are again based on a 3D structure, with a BET SSA around  $100-150 \text{ m}^2/\text{g}$  and a relatively large pore volume.



**Figure 6.** Cyclic voltammetry (CV) curves obtained from  $mNiMn_2O_x$ -600 (**a**) and  $mNiCoMnO_4$ -800 (**b**) electrode with different scan rates (1 to 100 mV/s) in 0.1 mol/L  $Na_2SO_4$  at room temperature [63,64]. Reprinted with permission from The Royal Society of Chemistry.

Nanoporous carbons are intensively investigated as catalysts that are expected to be highly active in ORR. They are usually highly porous with large accessible surface area, high conductivity and stability, and offer large interfacial area for the reactions, faster charge transport and short diffusion path for the oxygen gas. All these appealing properties make ordered mesoporous carbons (OMC) prospective catalysts for ORR. Doping carbon with N, P, S, or metal atoms is a common way to improve their catalytic activity. Unfortunately, the synthesis of a transition metal- and nitrogen co-doped mesoporous carbon (M-N-MC) is challenging using a classical nanocasting approach due to the limitations associated with the precursors, e.g., poor solubility of metal-macrocyclic complexes in most solvents and poor wettability of the precursor solution on the pore surface of the silica template [66]. Nevertheless, Tang et al. [66] reported a novel pathway to do this, i.e., the sublimation and capillary-assisted nanocasting method (SCANC). In this work, SBA-15 silica was used as a template and metallophthalocyanines (MPc, wherein M = Fe, Co, Ni or Cu) were used as carbon precursors. The authors compared the catalytic activity of Fe-N-MC pyrolized at different temperatures and once the optimal one was found, i.e., 700 °C, they synthesized M-N-MC with different metals and compared their catalytic activities. Elemental analysis, XPS and XRD showed that all elements were uniformly distributed throughout the porous carbon framework for Fe-N-MC obtained at 700 °C. This particular OMC exhibited a highly ordered porous structure with high SSA (988 m<sup>2</sup>/g), narrow pore size distribution (3.5 nm) and large pore volume ( $0.87 \text{ cm}^3/\text{g}$ ). Electrochemical tests were carried out in a standard three-electrode cell with coated RDE as a working electrode, Ag/AgCl or Hg/HgO and nickel mesh as a reference and counter electrodes, respectively. Finally, a cell with a serpentine flow field with gas diffusion electrode was used as a working electrode. All M-N-MC demonstrated an excellent activity towards ORR. It is to be noted that for the first time, to the best of our knowledge, a nanocast catalyst based on non-noble metals, i.e., Fe-N-MC-700, exhibited substantially better ORR activity compared to commercial Pt/C. More importantly, the great potential of these catalysts in rechargeable zinc-air battery applications was established. Song et al. [67] performed a one-step synthesis of sulfur and nitrogen co-doped OMC using SBA-15 silica as a template. The resulting SN-OMC material pyrolyzed at 900 °C reached high catalytic activity towards ORR, being comparable to commercial Pt/C catalysts, with a preferable 4-electron reaction process. Moreover, the samples showed excellent stability during 40,000 s (with an excellent remaining current density of 93%), which was far better than the commercial Pt/C catalyst (77% remained). However, so far, all reported studies used SBA-15 silica, a mainly 2D pore structure, as the starting template. Considering the results discussed above, it would appear beneficial to use a material with a 3D pore network and relatively large mesopore size and pore volume as a template, such as KIT-6 silica.

#### 2.4. Advantages and Limitations of Nanocast Electrocatalysts

One of the most appealing aspects of the nanocasting technique is the ability to synthesize highly versatile nanoporous non-silica materials with tunable properties. Such materials are often quite difficult to produce using classical direct synthesis or soft-templating approaches, whereby dense oxide particles may rapidly form and grow to large crystals leading to low surface area materials. The nanocasting approach allows synthesizing materials with complex chemical compositions and precise stoichiometry, e.g., mixed metal spinels, perovskites, and other complex phases, while restricting the final product to the nanoscale thanks to the silica/carbon mold acting as a physical growth inhibiter. Moreover, it is also possible to control the final pore topology of the nanocast electrocatalysts via the variation of the parent mold dimensionality, i.e., using a material with a 2D vs a 3D pore system as a mold. Following this approach, one may thus easily synthesize ordered nanocast replicas or isolated nanoparticles with specific morphologies, e.g., nanorods [68–70]. It is also possible to tune the physico-chemical properties of the replicas, i.e., specific surface area, pore volume and pore size, by adjusting the pore size and other physico-chemical parameters of the parent mold as well as the amount of metallic precursor introduced. Finally, if performed properly, the nanocasting may also allow the replication of the particle shape and size of the parent material, allowing a finer control on the resulting nanocast that may be of importance for high-end applications that require specific particle size and shapes, e.g., nanospheres vs. microparticles. Overall, among all the synthesis methods available, the nanocasting route remains one of the most interesting to create complex nanostructured electrocatalysts. However, such versatility is associated with important limitations that must be taken into account, and that would need to be overcome in order to start considering this method as potentially interesting for industrially relevant procedures. The first major limitation is the amount and complexity of steps involved within the nanocasting process. It is a time and energy consuming procedure that involves three major steps: the impregnation of the mold, the thermal/chemical conversion of the precursors and the chemical/thermal removal of the mold. Due to the potential complexity of the procedures, it is also relatively hard, depending on the system, to scale-up efficiently the overall nanocasting procedure. The very large majority of studies discussed in this review and presented in the literature were performed at a research laboratory scale with only few grams of samples being synthesized. In order to produce an industrially relevant material, at least for a pilot-plant system and putting aside all the formulation issues, one must be able to produce hundreds of kilograms on a daily/weekly basis. Even if it would be technically possible for relatively simple system such

as mCo<sub>3</sub>O<sub>4</sub>, it would end up in an extremely costly material. A second potential drawback is the chemical compatibility between the mold and the envisioned nanocast oxide. One must select a mold that is easily and selectively removable while the nanocast electrocatalyst remains unaffected. Considering that the vast majority of molds are mesoporous silica or carbon materials and the fact that they are removed with concentrated sodium hydroxide or hydrofluoric acid solutions and/or thermal treatments, it limits the choice of usable oxides. Finally, nanocast electrocatalysts are highly porous systems, which is undoubtedly an advantage from the surface reaction point of view but might also impose some limits regarding the mechanical/structural stability of the materials, especially when cycled many times under electrical potential. Therefore, one must monitor the evolution and stability of the nanostructured architecture over time.

#### 3. Conclusions and Outlook

Effective mesoporous electrocatalysts for oxygen reduction and oxygen evolution reactions can be synthesized using the nanocasting route. This versatile approach has many benefits over other pathways, especially regarding the structuring/ordering of complex nanoporous architectures. In general, ordered mesoporous silica materials are the templates of choice and among this vast family, mainly two different types are used: MCM-41 and SBA-15 that exhibit a pore structure made out of a 2D arrangement of cylindrical pores, and MCM-48 and KIT-6 where the 3D pore architecture is constituted by two interwoven mesoporous subnetworks following a gyroid-like structure. In most studies reported so far, SBA-15 and KIT-6 are preferred since they are the large pore analogues of MCM-41 and MCM-48, respectively, and therefore allow easier infiltration and impregnation steps. Moreover, KIT-6 silica is often preferred as a template owing to its native 3D interconnected pore network, which was found to be beneficial for the activity and the durability/cyclability of the resulting electrocatalysts.

With regard to the porosity characteristics of the electrocatalysts, regardless of the chemical composition, it was clearly observed that higher specific surface areas led to higher activity due to a larger number of active sites being exposed on the surface of the catalysts, ultimately resulting in an increased ECSA. In contrast, the effects of the pore size are not so straightforward to evaluate. In general, there is no direct correlation between the mesopore size of the parent ordered mesoporous template and the resulting nanocast replica. However, it remains that a "fairly large mesopore size" for the nanocast, i.e., about 7–10 nm, leads to promising electrochemical activity. The role of the total pore volume, on the other hand, is however, unambiguous. A higher pore volume is commonly associated with an enhanced mass transfer, ultimately providing higher activity.

Regarding the chemical composition of the nanocast catalysts, one of the main strategies to increase their conductivity and activity is to use a combination of transition and/or noble metals to dope/modify mesoporous (mixed) metal oxides. From the available literature, the ideal weight percentage of the dopant should not be higher than 10%. Indeed, higher loadings were generally associated with a loss of activity. Nowadays, the most common composition used as basis for doped nanocasts is mesoporous cobalt oxide ( $mCo_3O_4$ ). Especially, doping with electron-rich metals, e.g., Au, Pd, and Fe, enhances significantly the electrocatalytic activity compared to the pure mCo<sub>3</sub>O<sub>4</sub>. In terms of phases and crystallinity, spinel systems are seen as more promising materials. However, it was also reported that some doped metal oxides could outperform pure spinel phases. Therefore, one can expect that the most desirable design has not yet been determined, and more research needs to be carried out to fully elucidate the most potent material. Synergistic effects between metals are also an important factor affecting the electrocatalytic performance of the materials, but here as well, it is still not fully established and understood. More systematic and comprehensive studies are needed especially for two- and three-metal spinels or doped mixed metal oxides. Furthermore, even if very few reports are available so far, it appears that the combination of metals and (nanostructured) carbon is highly desirable to further increase the conductivity and the specific surface area of the nanocast catalysts, ultimately resulting in enhanced reaction kinetics and potentially improved catalytic and cycling stability. Such design of electrocatalysts would then need to be tested in Li–air/O<sub>2</sub> cells, for instance, and their stability over charge/discharge cycles validated, especially regarding the Li<sub>2</sub>O<sub>2</sub> formation/decomposition processes.

One of the most interesting aspects of electrocatalysts observed in this review is the defective structure. Despite the lack of systematic studies for various compositions on the topic, defects were found to improve the kinetics of the oxygen evolution and reduction reactions. Oxygen vacancy sites are believed to be the main adsorption sites for the reaction species of OER and can thus provide improved activity. Therefore, the role of defects, especially oxygen or metal ions vacancies, is a subject of great interest, and a systematic approach in the investigation of their effects on the electrocatalytic properties of metal oxides is a necessity.

Finally, one of the big question marks is the role of the pore ordering. Many catalysts discussed in this short review did exhibit some order. However, some samples showed almost no order and were still very promising as electrocatalysts for OER and/or ORR. Therefore, it would be of prime interest to clearly establish the role of the mesostructure and to evaluate its necessity for long-term durability and cyclability. This latter point is critical since the major drawbacks of the nanocasting procedure are its costs, the difficult scale-up and the substantial amount of time and steps necessary to obtain the replica. If the pore ordering is not mandatory, it would open the way to other cheaper and scalable templates that may allow an easier casting process. Regardless of the next-generation catalysts, one should remember that the aim is to produce an industrially relevant material, which allows the production costs to be minimized and working with relatively easy procedures with a minimum number of synthesis steps.

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#### Abbreviations

2D	two-dimensional
3D	three-dimensional
3DOM	three-dimensional ordered mesoporous
BET	Brunauer-Emmett-Teller method
BJH	Barrett-Joyner-Halenda method
CE	counter electrode
CV	cyclic voltammetry
ECSA	electrochemical surface area
EXAFS	extended X-ray absorption fine structure
GC	glassy carbon
GE	gold electrode
HER	hydrogen evolution reactions
LSV	linear sweep voltammetry
m	mesoporous
MABs	metal-air batteries
MC	mesoporous carbon
NPs	nanoparticles
OER	oxygen evolution reaction
OMC	ordered mesoporous carbons
ORR	oxygen reduction reaction
RDE	rotating disk electrode
RE	reference electrode
RFCs	reversible fuel cells
RHE	reversible hydrogen electrode

RRDE	rotating ring disk electrode
SCANC	sublimation and capillary-assisted nanocasting method
SCE	saturated calomel electrode
SEM	scanning electron microscopy
SSA	specific surface area
STL	spent tea leaves
TEGDME	tetraethyleneglycoldimethylether
TEM	transmission electron microscopy
WE	working electrode
XANES	X-ray absorption near edge structure
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZABs	zinc-air batteries

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