DOI: 10.1002/celc.201901584

Full Paper

Received: 25. September. 2019

Revised: 12. November 2019

Accepted Article published: 29. November 2019

Electrocatalysis of Oxygen on Bifunctional Nickel-Cobaltite Spinel

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<spi> An invited contribution to a Special Collection dedicated to Giornate dell'Elettrochimica Italiana 2019 (GEI2019)

carbon nanofibers

spinel

oxygen reduction

oxygen evolution

bifunctional oxygen electrodes

Spin me round: Transition-metal-based materials are among the most active and durable catalysts for the effective electrocatalysis of oxygen-related reactions. NiCo_2O_4 spinel supported on electrospun carbon nanofibers presents good performance and bifunctionality for both the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Oxidized species (Ni^{3+} and Co^{3+}) enhance OER, whereas lower oxidation states (Ni^{2+} , Co^{2+} , Ni^0 and Co^0) enhance ORR.

Transition-metal-based materials are among the most active and durable catalysts for the effective electrocatalysis of oxygen-related reactions. Herein, we present a study on bifunctional catalysts as air electrodes aimed at metal-air batteries based on nickel and cobalt spinel (NiCo_2O_4) supported on electrospun carbon nanofibers. The physicochemical features of these transition-metal-based catalysts are essential for the understanding of their electrochemical activity. Results show that the major presence of oxidized Ni and Co species (Ni^{3+} and Co^{3+}) produces higher activity for the oxygen evolution reaction (OER), whereas lower oxidation states of the metals (Ni^{2+} , Co^{2+} , Ni^0 and Co^0) together with the presence of N-doped carbon lead to enhanced oxygen reduction reaction (ORR) performance. This study highlights the importance of designing catalysts in terms of crystallographic structure and proper oxidation states of the elements for maximizing their performance.

1. Introduction

A new way to produce and store electrical energy is necessary to address future energy demands and reduce polluting emissions.^[1,2] Rechargeable alkaline metal-air batteries can be considered one of the most promising next energy systems owing to their extremely high energy densities.^[3--7] These make them particularly interesting for applications in electrical-energy storage systems for coupling intermittent renewable energy sources into smart energy grids. However, this kind of batteries requires very efficient and durable bifunctional electrocatalysts to accelerate the kinetics of oxygen reduction reaction (ORR), taking place during the discharge, and oxygen evolution reaction (OER), occurring during charging of the battery.^[8--12] Nowadays, the state-of-the-art catalysts are Pt-based nanoparticles for the ORR

and IrO_2 for the OER.^[13--15] However, the high cost of these electrocatalysts makes these materials unattractive. To replace these expensive noble catalysts, low cost alternatives such as transition metal oxides have been considered.^[16--22] Among them, cobalt-based oxides are envisaged as the most active catalysts for the electrocatalysis of oxygen.^[23--30] Spinel-type Co_3O_4 nanoparticles have received a great deal of attention as bifunctional materials for oxygen reactions due to their higher intrinsic activity (compared to noble metals) and suitable stability, in particular for the OER.^[25,26,31,32] However, the electrical conductivity of these materials is not appropriate for the application in metal-air batteries. Ni and other transition metals can partially replace Co atoms in the Co_3O_4 spinel structure introducing electronic levels in the band gap, improving in such a way its electronic conductivity while promoting water electro-adsorption and oxygen evolution.^[33--37] Another approach is supporting transition metals on conductive and graphitic carbon nanomaterials, in order to maintain suitable stability under cycling operation. In fact, composite catalysts based on transition metal oxides and carbon (in particular, nitrogen-doped carbonaceous material) have received increasing attention owing to their synergistic catalytic activity.^[33,38--42] Recently, our group investigated electrospun carbon nanofibers (CNF) decorated with both cobalt oxide and metallic cobalt ($\text{CoO} \langle \text{C} \rangle \text{Co/CNF}$)^[25] or loaded with nickel and cobalt (both in the metallic and oxide forms),^[43] as bifunctional air electrodes, which presented good reversibility and stability. In the present research the latter catalyst (NiCo-loaded CNFs),^[43] was further oxidized with the aim of synthesizing the pure spinel structure (NiCo_2O_4) supported on the electrospun CNFs. The performance for the oxygen electrocatalysis (i.e., water splitting and oxygen reduction) of the catalyst was evaluated and compared to the previously reported NiCo-loaded CNF catalyst in order to elucidate the performance as a function of the oxidation state and the crystallographic structure of Ni $\langle \text{C} \rangle$ Co based materials.

2. Results and Discussion

The XRD pattern of NiCo₂O₄/CNF (Figure¹) shows characteristic diffraction peaks of a cubic spinel structure (JCPDS card No: 01073-1702). A peak centered at $2\theta = 26.3^\circ$ is ascribed to the (002) plane of graphitic carbon.^[44,45] The NiCo₂O₄ crystallite size, calculated by the Scherrer's equation, is about 12 nm.

The TG/DSC profiles of electrospun NiCo-loaded CNF are shown in Figure² with the only purpose to elucidate the selected oxidation temperature to obtain NiCo₂O₄/CNF. A large weight loss of about 60% in the temperature range 400--500 °C is due to the decomposition of carbon nanofibers. Therefore, we considered the temperature value of 350 °C suitable for the thermal oxidation treatment of electrospun NiCo-loaded CNF avoiding the decomposition of carbon nanofibers structure. The TG/DSC analysis profile of NiCo₂O₄/CNF is also reported in Figure² in order to evaluate the amount of NiCo₂O₄ in the composite material. The TG curve shows a significant weight loss (about 60 wt%) associated to an exothermic peak in the temperature range 320--400 °C due to the complete oxidation of carbon nanofibers. The amount of residual NiCo₂O₄ in the composite material is about 40 wt%.

Figure³ shows TEM images and the particle size distribution of the electrospun spinel NiCo₂O₄/CNF. The image at a lower magnification (Figure³) shows the presence of porous carbon nanofibers with well-distributed NiCo₂O₄ nanoparticles. The diameter of the nanofibers is in the range of 100--200 nm. The higher magnification images (Figure³) further confirm the good dispersion of NiCo₂O₄ nanoparticles in the graphitic matrix of carbon nanofibers. The lattice fringes, indicated in Figure³ , can be indexed to the (111) crystal plane of NiCo₂O₄ as also revealed by XRD. The particle size distribution was obtained by calculating the particle average diameter of one hundred selected particles (Figure³) . The peak value of the distribution

curve was taken as an average particle size of about 12 nm, in agreement with the value obtained from XRD.

The textural properties of NiCo₂O₄/CNF were investigated by N₂ physisorption, recording the adsorption/desorption isotherms and using the Brunauer-Emmett-Teller (BET) method to calculate the surface area (S_{BET}). The S_{BET} and total pore volume were about 153 m²·g⁻¹ and 0.311 cm³·g⁻¹, respectively. The lower surface area of NiCo₂O₄/CNF compared to the NiCo-loaded CNF (309 m²·g⁻¹) could be attributed to the thermal treatment at 350 °C in air which leads to particle agglomeration as well as to a carbon loss (the amount of residual carbon for the present catalyst after the thermal treatment is about 40% compared to 20% of the NiCo-loaded CNF starting material).

X-ray photoelectron spectroscopy (XPS) measurements were performed in order to investigate the surface composition and oxidation state of the species forming the electrospun NiCo₂O₄/CNF. Table 1 reports the atomic concentrations of C1s, N1s, O1s, Co2p and Ni2p. The Ni/Co atomic ratio is about 0.5 and the sum of the Co/O and Ni/O atomic ratios is about 0.76 in accordance with the NiCo₂O₄ stoichiometric compound. The nitrogen species were slightly more abundant in the spinel type material than in the NiCo-loaded CNF sample.

Figure 4 shows the XPS deconvolution curves of the O1s, C1s and N1s orbitals for the NiCo₂O₄/CNF spinel material. The curve fitting of O1s spectrum (Figure 4a) presents five peaks. The first peak centered at 529.5 eV can be attributed to the metal-oxygen bonds (M-O). The peak at 530.5 eV indicates the presence of hydroxyl groups (-OH) on the surface of NiCo₂O₄/CNF. The peak at 531.5 eV is due to the presence of oxygen ions (O²⁻) in low coordination at the surface. A further peak centered at 532.5 eV could be ascribed to the presence of adsorbed water on the surface.^[46] The presence of C-OH phenolic groups was recorded at 533.6 eV.^[43]

The deconvolution analysis of C1s spectrum leads to five peaks (Figure⁴) corresponding to different carbon species. The main peak at 284.6 eV is normally ascribed to graphitic carbon (C=C sp²) while the peak at 285.5 eV is attributed to amorphous carbon (C-C sp³). The peaks at 286.5 eV and 287.6 eV can be associated with species of carbon bonded to oxygen and nitrogen species designated as C-C-O/C-C-N and C=C-O/C=C-N, respectively. The smaller peak at 289.6 eV is probably due to the presence of carboxyl groups (O=C-C-O) on the surface.^[47]

The N1s spectrum (Figure⁴) was deconvoluted in five peaks which can be associated to different nitrogen species such as the pyridinic-N (398.2 eV), pyrrolic-N (400.1 eV), graphitic-N (401.4 eV) and pyridine-N-oxide (402.7 eV).^[48] A further peak at about 399 eV indicates the presence of Co-C-N_x type species. Figure⁴ d reports a histogram of the nitrogen contents in both NiCo₂O₄/CNF and NiCo-loaded CNF samples. It should be noted that the NiCo₂O₄/CNF has a higher amount of nitrogen in the form of pyridinic-N, graphitic-N and Co-C-N_x with respect to NiCo-loaded CNF sample. These nitrogen groups are considered as ORR active sites.

In Figure⁵ the deconvolution spectra of Ni2p and Co2p orbitals are shown. The deconvolution of Ni2p spectrum (Figure⁵) shows six peaks. The peaks at 854.5 and 871.5 eV are attributed to Ni²⁺ ions located in the octahedral sites of the spinel structure while the peaks at 856.1 and 873.8 eV are assigned to Ni³⁺ ions.^[49] Moreover, two “shake-up” satellite peaks can be identified at binding energies of 862 and 880 eV. These satellite peaks were fitted considering only one broad line but include the contribution of both Ni²⁺ and Ni³⁺ ions.^[50] As reported in Figure⁵ , the Ni³⁺ ions are present in larger amount with respect to the Ni²⁺ ions, indicating that many active sites could be available for the OER. The Co2p spectrum (Figure⁵) was fitted in nine deconvolution peaks. The peaks at 779.5 and 795 eV are ascribed to the Co³⁺ ions while the peaks at 780.5 and

796 eV are due to the presence of Co^{2+} ions. Two “shake-up” satellite peaks are also evident in the $\text{Co}2p$ spectrum at a binding energy of about 787 eV and 803 eV. Each satellite peak can be deconvoluted in two peaks due to the contribution of Co^{3+} and Co^{2+} ions.^[51] A further peak at about 782 eV can be associated with species of cobalt bonded to nitrogen ($\text{Co} < \text{C} - > \text{N}_x$). In Figure 5 the amount of Co species present in $\text{NiCo}_2\text{O}_4/\text{CNF}$ are reported. It is possible to observe that the Co^{2+} ions are in excess with respect to the Co^{3+} ions. As known, Co^{2+} ions play a fundamental role in the ORR catalytic process.^[47]

Figure 6 depicts the linear sweep voltammetry (LSVs) recorded in the GDWE in comparison with the NiCo-loaded CNF catalyst, studied in our previous work,^[43] and a noble metal-based catalyst,

Pd/Vulcan, synthesized as described elsewhere,^[15] used as a reference material. The loading on the working electrode was the same for the three catalysts, 0.5 mg cm^{-2} of the active material (NiCo, NiCo_2O_4 or Pd).

2.1. Oxygen Reduction Reaction

The two non-noble catalysts present similar performances for the oxygen reduction reaction (ORR), Figure 6a, whereas, as expected,

Pd/Vulcan presents the highest activity showing the best onset potential, $E_{\text{onset}} = 0.930 \text{ V}$ vs. RHE, as can be also ascertained from Table 2.

Both NiCo-based materials exhibit very similar onset potential (0.887 V for NiCo-loaded CNF and 0.861 V $\text{NiCo}_2\text{O}_4/\text{CNF}$), around 40–70 mV lower than the one for Pd/Vulcan. This means that the overpotential for the ORR in the case of the noble metal catalyst is the lowest (300 mV, versus 343 mV and 369 mV for the NiCo-based species, NiCo-loaded CNF and $\text{NiCo}_2\text{O}_4/\text{CNF}$, respectively). The differences in activity can be ascribed to different aspects. First, the best performance of the Pd/Vulcan is due to the best

intrinsic activity of the noble metal towards this reaction, in comparison to the catalysts based on non-noble transition-metals. Among the two NiCo-based materials, taking into account that the two catalysts show a similar crystallite size ($10\text{--}11\text{ nm}$ for the NiCo-loaded CNF and 12 nm for the NiCo_2O_4), the different oxidation state for Ni and Co and the crystallographic structure can be the cause for the diverse catalytic activity. NiCo-loaded CNF catalyst presents a higher concentration of Co^{2+} ions (63% versus 51% for $\text{NiCo}_2\text{O}_4/\text{CNF}$), recognized as active sites favoring the ORR.^[46] Besides, the presence of both cobalt and nickel in their metallic form in the NiCo-loaded CNF is also responsible for the slightly enhanced activity for the ORR, as they participate as secondary active sites.^[43]

2.2. Oxygen Evolution Reaction

The performance regarding the oxygen evolution reaction (OER) shows significant differences between the three catalysts. The spinel type material shows the highest activity for the OER, with a potential at 10 mA cm^{-2} of 1.453 V vs. RHE (meaning an overpotential of 223 mV). This is one of the lowest values obtained within the current literature, although a straightforward comparison is not always feasible. For example, Bae et al. obtained NiCo nanowires grown on a carbon fiber woven fabric.^[52] Their NiCo-based material showed an overpotential of 302 mV for the OER in a 1 M KOH solution. Yan et al. also tested NiCo-nanowires deposited onto a nickel foam as a catalyst for the OER in a 1 M KOH solution,^[53] with an overpotential for the OER of 337 mV . Han et al. produced an excellent review on transition metals (Co, Ni, and Fe) electrocatalysts for the water oxidation reaction.^[37] Our $\text{NiCo}_2\text{O}_4/\text{CNF}$ spinel material presents the lowest overpotential for the OER within those cited in their review. Surendran et al. determined that functionalizing nanostructured carbon nanofibers (CNFs) with bimetallic phosphides produces active electrodes for several reactions (oxygen reduction, oxygen evolution and hydrogen evolution).^[54] In particular, these authors developed NiCoP nanoparticles

encapsulated in electrospun CNFs, with a current density towards the oxygen evolution reaction of 10 mA cm^{-2} at a very low overpotential of 268 mV . In this work, authors performed a comparative analysis of other studies in literature. Our NiCo_2O_4 -spinel is within the best catalysts presented, excluding PtNi/CNF . Nonetheless, the measuring conditions of our experiment differ from the ones reported, generally RDE measurements either in 0.1 or 1 M KOH solutions, although there are some works employing foams, or carbon papers; accordingly, as previously stated, this comparison is not entirely straightforward but can be considered as a good estimation.

The $\text{NiCo}_2\text{O}_4/\text{CNF}$ catalyst is clearly a superior oxygen evolution catalyst in comparison to the previously reported NiCo-loaded CNF, with an overpotential of 290 mV . As expected, the noble metal-based catalyst is not as good for the evolution of oxygen as the transition metal-based catalysts, but still presents a lower overpotential value (295 mV) in comparison to other catalysts reported in literature^[37]

The difference between $\text{NiCo}_2\text{O}_4/\text{CNF}$ and NiCo-loaded-CNF resides in the extended oxidation range for the spinel type material, leading to an increase in Ni^{3+} and Co^{3+} ions for the NiCo_2O_4 . The Ni^{3+} ions are present in larger amount with respect to the Ni^{2+} ions indicating that many active sites are available for the OER. Co^{3+} ions are also responsible for a preferred absorption of $\text{OH}^{<\text{M}>}$ anions, acting as active species for the OER.^[4] Besides, it should be noted that the $\text{NiCo}_2\text{O}_4/\text{CNF}$ has a higher amount of nitrogen in the form of pyridinic-N. Bin et al. determined that N in the form of pyridinic species accepts electrons from adjacent C atoms.^[55] This facilitates the adsorption of $\text{OH}^{<\text{C}>}$ and $\text{OOH}^{<\text{C}>}$ (water oxidation intermediates), being the rds (rate-determining step) for OER in basic media.

In summary, the active sites in these catalysts could be several, depending on the reaction involved. In the case of metal sites, those are different for the ORR and the OER. Ni^{2+} and Co^{2+} , along with Ni^0 and Co^0 , are more active for the ORR; whereas, Ni^{3+} and Co^{3+}

promote the OER. Regarding N-sites, it is believed that pyridinic N is active for both reactions (OER and ORR), whereas graphitic N seems active only in the case of the ORR, along with Co<C->Nx.

2.3. Bifunctional Behavior and Durability

A proper rechargeable air electrode must present a good reversibility, in order to carry out both reactions with the lowest difference in the potential. The difference between the onset potential for both reactions (ORR and OER) indicates the reversibility (i.e. bifunctional behavior of a catalytic system). This value, referred in literature as ΔE , has been widely employed in the specific literature for bifunctional electrodes. The spinel material shows the best reversibility of the three studied systems (see Table²): ΔE for NiCo₂O₄/CNF was 523 mV, followed by Pd/Vulcan with ΔE equal to 595 mV. The reversibility of the NiCo-loaded CNF was as high as $\Delta E=633$ mV.

Bifunctionality is a desired property in some systems such as regenerative fuel cells or metal-air batteries, but also durability is a key parameter in the lifetime of these devices. The stability of the catalyst was assessed at constant current (-80 mA cm^{-2}) for 24 h, as depicted in Figure⁷, in comparison to the NiCo-loaded CNF catalyst. As ascertained from the graph, the behavior for the NiCo-loaded CNF is more stable and with a more positive potential than for the spinel material. The initial decay in potential for the NiCo₂O₄/CNF catalyst could be due to the corrosion of carbon nanofibers, which are less graphitic and more porous than the CNF loaded with NiCo reported for comparison. In fact, the oxidative treatment at 350 °C in air, carried out on the catalyst in order to obtain the spinel structure (see the experimental section), caused the partial degradation of the graphitic carbon structure (as clearly visible in the TEM image at low magnification, Figure³a).

However, after the strong initial loss in the first hour, the decay is less pronounced with time, but still present during the 24^h test, indicating a lower stability of the spinel-based catalyst compared to the NiCo-loaded CNF. It is pointed out that the cause of this instability is not ascribed to the spinel structure but to the characteristics of the carbon support. Thus, an optimization of the preparation procedure, in order to obtain the spinel structure in a one-step synthesis, is necessary to obtain a more stable catalyst. This will be the object of a future work.

3. Conclusions

In the present manuscript, a nickel-cobaltite spinel supported on electrospun nanofibers was successfully synthesized. Its physical-chemical features were compared to those of a previously reported NiCo-loaded CNF, with the aim of analyzing the effect of the crystallographic structure and oxidation state of both Ni and Co on the performance as bifunctional catalyst. XPS analysis revealed the main differences among both samples: NiCo-loaded CNF presents Ni and Co both in the metallic and the oxide form (Ni^{2+} , Ni^{3+} and Co^{2+}), as well as N surface groups in the form of graphitic and pyridinic N. On the other hand, $\text{NiCo}_2\text{O}_4/\text{CNF}$ presented a higher amount of Ni^{3+} and Co^{3+} , and a higher amount of both graphitic and pyridinic N. Both catalysts presented similar performances for the oxygen reduction reaction. The main differences were encountered for the oxygen evolution reaction. The nickel cobaltite spinel showed an enhanced activity, due to the higher presence of Ni^{3+} and Co^{3+} groups, and a slight contribution from the higher amount of pyridinic N, also favoring this reaction. $\text{NiCo}_2\text{O}_4/\text{CNF}$ showed a low overpotential (at 10 mA cm^{-2}), 223 mV, what makes it an excellent water splitting catalyst. The nickel cobaltite spinel, supported on electrospun nanofibers, showed also a remarkable reversibility ($\Delta E = 592\text{ mV}$), so it could act as a good bifunctional catalyst, although durability must be still enhanced.

Experimental Section

Materials and Methods

Nickel (II) acetate tetrahydrate ($\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, Sigma Aldrich, 99.9%) and cobalt (II) acetate tetrahydrate ($\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, Sigma Aldrich, 99%) were used as metal precursors. Polyacrylonitrile (PAN, Sigma Aldrich, Mw= 150,000) was used as carbon nanofibers precursor. In our previous work,^[43] the synthesis procedure by electrospinning along with the thermal treatment are reported. In order to obtain $\text{NiCo}_2\text{O}_4/\text{CNF}$ in spinel structure form, a further thermal treatment at 350°C in static air for 1 h was performed.

Physicochemical Characterization

Physical-chemical characterization techniques were utilized to identify the morphological and structural properties of the synthesized material. X-ray diffraction (XRD) spectra were acquired by using a Philips X-pert 3710. Differential thermal analysis (DSC) and thermogravimetric (TG) analysis were carried out by using a 409°C NETZSCH-Gerätebau GmbH analyzer. X-ray photoelectron spectroscopy (XPS) analysis was obtained with a Physical Electronics (PHI) 5800-01 spectrometer. All the curve fittings were performed by the PHI Multipak 6.1 software. Transmission electron microscopy (TEM) was carried out using a FEI CM12 instrument. Surface area and pore size were determined by nitrogen adsorption at 77.3 K, from Brunauer-Emmet-Teller equation (BET) (ASAP 2020M Micrometrics).

Electrochemical Characterization

The electrochemical experiments were performed with an Autolab PGSTAT instrument with NOVA software package connected to a 3-electrode half-cell. The activity of $\text{NiCo}_2\text{O}_4/\text{CNF}$ towards the oxygen reduction reaction and the oxygen evolution reaction was tested in a gas diffusion electrode. There are not many works in literature using this type of working electrode, which acts as a bridge between the fundamental studies in rotating ring disk electrode and the final device.^[56--58] To this end, an ink of the catalyst was sprayed onto a carbon cloth with a gas diffusion layer (LT

1200WELAT, ETEK) and mounted in a gas diffusion working electrode, as described in ^[25] To prepare the ink, an amount of catalyst was weighed and dispersed in a solution of isopropanol and water, containing Nafion as a binder. The amount of catalyst in the ink was calculated so that the electrode had a loading of $0.5 \pm 0.02 \text{ mg cm}^{-2}$ of active phase (either NiCo_2O_4 , NiCo or Pd). The total amount of Nafion (5 wt.% solution) was 30 wt.% of the total ink. The evolution and reduction of oxygen were evaluated in a 6 M high purity KOH (Sigma-Aldrich, >90% purity, used as received) solution flowing either N_2 or O_2 (respectively). The stability of the catalyst was evaluated at constant current of 80 mA cm^{-2} for 24 h, evaluating the potential decay with time.

Acknowledgements

The research leading to these results has received funding from the “Accordo di Programma CNR-MiSE, Gruppo tematico Sistema Elettrico Nazionale e Progetto: Sistemi elettrochimici per l'accumulo di energia”.

Conflict of Interest

The authors declare no conflict of interest.

<lit1><jnl>T. M. Gür, *Energy Environ. Sci.* **2018**, *11*, 2696--2767</jnl>.

<lit2><jnl>C. Lo Vecchio, A. S. Aricò, G. Monforte, V. Baglio, *Renewable Energy* **2018**, *120*, 342--349</jnl>.

<lit3><jnl>T. Sadhasivam, K. Dhanabalan, S.-H. Roh, T.-H. Kim, K.-W. Park, S. Jung, M. D. Kurkuri, H.-Y. Jung, *Int. J. Hydrogen Energy* **2017**, *42*, 4415--4433</jnl>.

<lit4><jnl>Y.-J. Wang, B. Fang, X. Wang, A. Ignaszak, Y. Liu, A. Li, L. Zhang, J. Zhang, *Prog. Mater. Sci.* **2018**, *98*, 108--167</jnl>.

<lit5><jnl>S. Altmann, T. Kaz, K. A. Friedrich, *Electrochim. Acta* **2011**, *56*, 4287--4293</jnl>.

- <lit6><jnl>B. Paul, J. Andrews, *Renewable Sustainable Energy Rev.* **2017**, 79, 585--599</jnl>.
- <lit7><jnl>X. Zhang, X. Cheng, Q. Zhang, *J. Energy Chem.* **2016**, 25, 967--984</jnl>.
- <lit8><jnl>S. Dresp, P. Strasser, *ChemCatChem* **2018**, 10, 4162--4171</jnl>.
- <lit9><jnl>R.[^]D. McKerracher, H.[^]A. Figueredo-Rodríguez, J.[^]O. Avila-Alejo, K. Kwasnicki, C.[^]P. De[^]León, C. Alegre, V. Baglio, A.[^]S. Aricò, F.[^]C. Walsh, *J. Electrochem. Soc.* **2018**, 165, A1254--A1262</jnl>.
- <lit10><jnl>S.[^]A. Grigoriev, P. Millet, K.[^]A. Dzhus, H. Middleton, T.[^]O. Saetre, V.[^]N. Fateev, *Int. J. Hydrogen Energy* **2010**, 35, 5070--5076</jnl>.
- <lit11><jnl>V. Neburchilov, H. Wang, J.[^]J. Martin, W. Qu, *J. Power Sources* **2010**, 195, 1271--1291</jnl>.
- <lit12><jnl>P. Clechet, C. Martelet, J.[^]R. Martin, R. Olier, *Electrochim. Acta* **1979**, 24, 457--461</jnl>.
- <lit13><jnl>Y. He, J. Zhang, G. He, X. Han, X. Zheng, C. Zhong, W. Hu, Y. Deng, *Nanoscale* **2017**, 9, 8623--8630</jnl>.
- <lit14><jnl>J.[^]C. Cruz, V. Baglio, S. Siracusano, R. Ornelas, L.[^]G. Arriaga, V. Antonucci, A.[^]S. Aricò, *Int. J. Hydrogen Energy* **2012**, 37, 5508--5517</jnl>.
- <lit15><jnl>C. Alegre, A. Stassi, E. Modica, C. Lo[^]Vecchio, A.[^]S. Aricò, V. Baglio, *RSC Adv.* **2015**, 5, 25424--25427</jnl>.
- <lit16><jnl>E. Antolini, *ACS Catal.* **2014**, 4, 1426--1440</jnl>.
- <lit17><jnl>A. Paulraj, Y. Kiros, M. Göthelid, M. Johansson, A.[^]R. Paulraj, Y. Kiros, M. Göthelid, M.[^]B. Johansson, *Catalysts* **2018**, 8, 328</jnl>.

- <lit18><jnl>J.-I. Jung, M. Risch, S. Park, M.[^]G. Kim, G. Nam, H.-Y. Jeong, Y. Shao-Horn, J. Cho, *Energy Environ. Sci.* **2016**, 9, 176--183</jnl>.
- <lit19><jnl>D. Chen, C. Chen, Z.[^]M. Baiyee, Z. Shao, F. Ciucci, *Chem. Rev.* **2015**, 115, 9869--921</jnl>.
- <lit20><jnl>C. Alegre, E. Modica, A.[^]S.[^]S. Aricò, V. Baglio, *J. Electroanal. Chem.* **2016**, 808, 412--419</jnl>.
- <lit21><jnl>M.[^]E. Hamzehie, L. Samiee, M. Fattahi, A.[^]A. Seifkordi, F. Shoghi, A. Maghsodi, *Renewable Energy* **2015**, 77, 558--570</jnl>.
- <lit22><jnl>Y. Cheng, S. He, J. Veder, R. De[^]Marco, S. Yang, S. Ping[^]Jiang, *ChemElectroChem* **2019**, 6, 3478--3487</jnl>.
- <lit23><jnl>A. Martínez-Lázaro, A. Rico-Zavala, F.[^]I. Espinosa-Lagunes, J. Torres-González, L. Álvarez-Contreras, M.[^]P. Gurrola, L.[^]G. Arriaga, J. Ledesma-García, E. Ortiz-Ortega, *J. Power Sources* **2019**, 412, 505--513</jnl>.
- <lit24><jnl>A. Aijaz, J. Masa, C. Rösler, W. Xia, P. Weide, A.[^]J.[^]R. Botz, R.[^]A. Fischer, W. Schuhmann, M. Muhler, *Angew. Chem. Int. Ed.* **2016**, 55, 4087--91</jnl>.
- <lit25><jnl>C. Alegre, C. Busacca, O. Di[^]Blasi, V. Antonucci, A.[^]S. Aricò, A. Di[^]Blasi, V. Baglio, *J. Power Sources* **2017**, 364, 101--109</jnl>.
- <lit26><jnl>D.[^]U. Lee, J.-Y. Choi, K. Feng, H.[^]W. Park, Z. Chen, *Adv. Energy Mater.* **2014**, 4, 1301389</jnl>.
- <lit27><jnl>S. Mao, Z. Wen, T. Huang, Y. Hou, J. Chen, *Energy Environ. Sci.* **2014**, 7, 609--616</jnl>.
- <lit28><jnl>J. Sanetuntikul, S. Hyun, P. Ganesan, S. Shanmugam, *J. Mater. Chem. A* **2018**, 6, 24078--24085</jnl>.

- <lit29><jnl>R. Gao, Y. Yin, F. Niu, A. Wang, S. Li, H. Dong, S. Yang, *ChemElectroChem* **2019**, 6, 1824--1830</jnl>.
- <lit30><jnl>H. Shui, T. Jin, J. Hu, H. Liu, *ChemElectroChem* **2018**, 5, 1401--1406</jnl>.
- <lit31><jnl>J. M. Luque-Centeno, M. V. Martínez-Huerta, D. Sebastián, G. Lemes, E. Pastor, M. J. Lázaro, *Renewable Energy* **2018**, 125, 182--192</jnl>.
- <lit32><jnl>Y. J. Sa, K. Kwon, J. Y. Cheon, F. Kleitz, S. H. Joo, *J. Mater. Chem. A* **2013**, 1, 9992</jnl>.
- <lit33><jnl>A. H. A. Monteverde Videla, P. Stelmachowski, G. Ercolino, S. Specchia, *J. Appl. Electrochem.* **2017**, 47, 295--304</jnl>.
- <lit34><jnl>X. Liu, M. Park, M. G. Kim, S. Gupta, G. Wu, J. Cho, *Angew. Chem. Int. Ed.* **2015**, 54, 9654--9658</jnl>.
- <lit35><jnl>M. Prabu, K. Ketpang, S. Shanmugam, *Nanoscale* **2014**, 6, 3173</jnl>.
- <lit36><jnl>D. Pletcher, X. Li, S. W. T. Price, A. E. Russell, T. Sönmez, S. J. Thompson, *Electrochim. Acta* **2016**, 188, 286--293</jnl>.
- <lit37><jnl>L. Han, S. Dong, E. Wang, *Adv. Mater.* **2016**, 28, 9266--9291</jnl>.
- <lit38><jnl>C. Yu, J. Lu, L. Luo, F. Xu, P. K. Shen, P. Tsiakaras, S. Yin, *Electrochim. Acta* **2019**, 301, 449--457</jnl>.
- <lit39><jnl>A. K. Samantara, S. Kamila, A. Ghosh, B. K. Jena, *Electrochim. Acta* **2018**, 263, 147--157</jnl>.
- <lit40><jnl>Z. Zhao, M. Li, L. Zhang, L. Dai, Z. Xia, *Adv. Mater.* **2015**, 27, 6834--6840</jnl>.
- <lit41><jnl>R. Wang, Z. Chen, N. Hu, C. Xu, Z. Shen, J. Liu, *ChemElectroChem* **2018**, 5, 1745--1763</jnl>.

- <lit42><jnl>P. Li, H. Jang, J. Zhang, M. Tian, S. Chen, B. Yuan, Z. Wu, X. Liu, J. Cho, *ChemElectroChem* **2019**, 6, 393--397</jnl>.
- <lit43><jnl>C. Alegre, E. Modica, A. Di[^]Blasi, O. Di[^]Blasi, C. Busacca, M. Ferraro, A.[^]S. Aricò, V. Antonucci, V. Baglio, *Renewable Energy* **2018**, 125, DOI 10.1016/j.renene.2018.02.089</jnl>.
- <lit44><jnl>M.-S. Wu, Y.-R. Zheng, G.-W. Lin, *Chem. Commun.* **2014**, 50, 8246</jnl>.
- <lit45><jnl>V. Ivanov, J.[^]B. Nagy, P. Lambin, A. Lucas, X.[^]F.[^]X.[^]B. Zhang, X.[^]F.[^]X.[^]B. Zhang, D. Bernaerts, G. Van[^]Tendeloo, S. Amelinckx, J. Van[^]Landuyt, *Chem. Phys. Lett.* **1994**, 223, 329--335</jnl>.
- <lit46><jnl>C. Zhang, T. Kuila, N.[^]H. Kim, S.[^]H. Lee, J.[^]H. Lee, *Carbon* **2015**, 89, 328-339</jnl>.
- <lit47><jnl>C. Alegre, C. Busacca, A. Di[^]Blasi, O. Di[^]Blasi, A.[^]S. Aricò, V. Antonucci, E. Modica, V. Baglio, *J. Energy Storage* **2019**, 23, 269--277</jnl>.
- <lit48><jnl>L. Zhang, Z. Su, F. Jiang, L. Yang, J. Qian, Y. Zhou, W. Li, M. Hong, *Nanoscale* **2014**, 6, 6590--6602</jnl>.
- <lit49><jnl>L. Qian, L. Gu, L. Yang, H. Yuan, D. Xiao, *Nanoscale* **2013**, 5, 7388</jnl>.
- <lit50><jnl>Y. Xue, Y. Wang, H. Liu, X. Yu, H. Xue, L. Feng, *Chem. Commun.* **2018**, 54, 6204--6207</jnl>.
- <lit51><jnl>J.[^]L. Gautier, E. Rios, M. Gracia, J.[^]F. Marco, J.[^]R. Gancedo, *Thin Solid Films* **1997**, 311, 51--57</jnl>.
- <lit52><jnl>S.-H. Bae, J.-E. Kim, H. Randriamahazaka, S.-Y. Moon, J.-Y. Park, I.-K. Oh, *Adv. Energy Mater.* **2017**, 7, 1601492</jnl>.

<lit53><jnl>X. Yan, K. Li, L. Lyu, F. Song, J. He, D. Niu, L. Liu, X. Hu, X. Chen, *ACS Appl. Mater. Interfaces* **2016**, 8, 3208--3214</jnl>.

<lit54><jnl>S. Surendran, S. Shanmugapriya, A. Sivanantham, S. Shanmugam, R. Kalai^{^^}Selvan, *Adv. Energy Mater.* **2018**, 8, 1800555</jnl>.

<lit55><jnl>H. Bin^{^^}Yang, J. Miao, S.-F. Hung, J. Chen, H.^{^^}B. Tao, X. Wang, L. Zhang, R. Chen, J. Gao, H.^{^^}M. Chen, *Sci. Adv.* **2016**, 2, e1501122</jnl>.

<lit56><jnl>R.^{^^}D. McKerracher, C. Alegre, V. Baglio, A.^{^^}S. Aricò, C. Ponce^{^^}de^{^^}León, F. Mornaghini, M. Rodlert, F.^{^^}C. Walsh, *Electrochim. Acta* **2015**, 174, 508--515</jnl>.

<lit57><jnl>X. Li, D. Pletcher, A.^{^^}E. Russell, F.^{^^}C. Walsh, R.^{^^}G.^{^^}A. Wills, S.^{^^}F. Gorman, S.^{^^}W.^{^^}T. Price, S.^{^^}J. Thompson, *Electrochem. Commun.* **2013**, 34, 228--230</jnl>.

<lit58><jnl>D. Sebastián, C. Alegre, M.^{^^}E. Gálvez, R. Moliner, M.^{^^}J. Lázaro, A.^{^^}S. Aricò, V. Baglio, *J. Mater. Chem. A* **2014**, 2, 13713</jnl>.

Table^{^^}1 Atomic concentration for C, N, O, Co and Ni.

Sample	C1 ^{^^} _s	N1 ^{^^} _s	O1 ^{^^} _s	Co ^{^^} _{2p}	Ni2p
NiCo ₂ O ₄ /C	70.	3.7	14.	7.5	3.8
NF	2		8		
NiCo-loaded/CNF	90.7	3.1	4.7	1.2	0.3

Table^{^^}2 Electrochemical parameters determined from LSVs: onset potential, overpotential, and reversibility ($\Delta E = E_{\text{OER}} - E_{\text{ORR}}$).

Catalyst	$E_{\text{ORR}}^{[a]}$	$\eta_{\text{ORR}}^{[b]}$	E_{OER}	$\eta_{\text{OER}}^{[b]}$	ΔE
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	[c]				
Pd/Vulcan	0.930	0.300	1.525	0.295	595
NiCo-loaded CNF	0.887	0.343	1.520	0.290	633
NiCo ₂ O ₄ /CNF	0.861	0.369	1.453	0.223	592

[a] Onset potential (V vs. RHE) for the ORR calculated at -- 1 mA cm^{-2} . [b] η overpotential for the ORR (V vs. RHE). [c] Potential for the OER calculated at -- 10 mA cm^{-2} .

Figure¹ NiCo₂O₄/CNF's XRD profile.

Figure² TG/DSC analysis patterns of both NiCo-loaded CNF (dotted line); NiCo₂O₄/CNF (solid line); (gas: air).

Figure³ TEM images (a--c) and particle size distribution (d) of NiCo₂O₄/CNF.

Figure⁴ XPS deconvolution curves of a) O1s, b) C1s, c) N1s orbitals for NiCo₂O₄/CNF and d) histogram of the corresponding nitrogen groups content in the NiCo₂O₄/CNF and NiCo-loaded CNF.

Figure⁵ XPS deconvolution curves of a) Ni2p orbitals, b) Co2p orbitals and c) histogram of the corresponding nickel and cobalt species content for NiCo₂O₄/CNF and NiCo-loaded CNF.

Figure⁶ LSVs for the NiCo-based materials in comparison to a noble metal-based catalyst, Pd/Vulcan A) ORR; B) OER. C) Overpotential at 10 mA cm^{-2} for the OER.

Figure⁷ Stability test for both NiCo-loaded CNF and NiCo₂O₄/CNF. Constant current = 80 mA cm^{-2} flowing O₂ in the electrolyte.