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Bifunctional oxygen reduction/oxygen evolution activity of mixed Fe-Co oxide nanoparticles with variable Fe:Co ratios supported on multi-walled carbon nanotubes

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We present a facile strategy for synthesis of Fe-Co mixed metal oxide nanoparticles supported on, and embedded inside high purity oxidized multi-walled carbon nanotubes (MWCNTs) of narrow diameter distribution as effective bifunctional catalysts able to reversibly drive the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR) in alkaline solutions. Variation of the Fe:Co ratio resulted in a pronounced trend in the bifunctional ORR/OER activity. Controlled synthesis and in-depth characterization enabled the identification of an optimal Fe:Co composition, which afforded a low OER/OER reversible overvoltage of only 0.83 V, taking the OER at 10 mA cm⁻² and the ORR at -1 mA cm⁻². Importantly, the optimal catalyst with a Fe:Co ratio of 2:3 exhibited very promising long-term stability with no evident change in the potential for both the ORR and the OER after 400 charge/discharge (OER/ORR) cycles at 15 mA cm⁻² in 6 M KOH. Moreover, detailed investigation of the structure, size and phase composition of the mixed Fe-Co oxide nanoparticles, as well as their localization (inside of or on the surface of the MWCNTs) revealed insight of the possible contribution of the individual catalyst components and their synergistic interaction on the catalysis.

Introduction

The fabrication of highly active and low cost bifunctional oxygen electrodes is a bottleneck for wide-spread utilization of renewable

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energy technologies such as unitized regenerative fuel cells (URFC) and metal-air batteries, such as Zn-air, Al-air and Li-air among others. The main challenge is to achieve high performance and reversibility of the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR), that are both kinetically sluggish and possess numerous intermediates. Moreover, the pH of the electrolyte drastically influences the performance of the catalyst due to shift in the potentials of the underlying intermediate reactions. For example, in the case of ORR, a high overpotential is required for the O₂/O₂⁻ redox couple (activation step) in acidic media. Only a few metals like Pt are active for the ORR at low pH conditions as they can provide the high free energy for O_2 adsorption.^[1] Other compounds such as transition metal oxides possess promising ORR activity in basic electrolytes due to the easier activation of oxygen molecules in alkaline media.^[2] Although the main focus is nowadays on transition metalheteroatom-doped carbon materials (e.g. Fe-N-C and Co-N-C^[3,4]), that are reported to be the most promising non-precious candidates for the ORR in alkaline media, metal oxides such as MnO_x, CoO_x, FeO_x (non-supported or supported on carbon) are also intensively studied for the oxygen reduction.^[5–8] The covalent interaction of metal oxides (such as CoO, Co₃O₄) with carbon supports often leads to dramatic electrocatalytic activity improvement in contrast to their non-carbon supported counterparts due to more efficient active site distribution coupled with improved conductivity of the catalytic film.^[9] Excellent ORR activity and long-term stability can be achieved through the design of hybrid oxides combining several transition metals. For example, spinel oxides based on Co₃O₄ with the Co atoms partially substituted by Ni, Cu, Mn and Fe show better ORR activity compared to the respective monometallic oxides.^[10-13] Tuning the morphology, crystallinity and composition of the catalyst nanoparticles as well as the properties of the carbon supports (oxidized or nitrogen (heteroatom)-doped carbon materials) makes it possible to approach the activity of commercial Pt-based benchmark ORR catalysts.^[3,5].

Similar considerations should be taken into account when designing non-precious OER electrocatalysts. It was shown that electrocatalysts based on compounds of transition metals (Co, Ni, Fe) such as oxides/hydroxides, perovskites/double perovskites as well as borides, phosphides and other compounds can serve as highly efficient systems for the OER in alkaline solutions.^[14,15] Unfortunately, many of these catalysts suffer from low electrical conductivity. However, forming intimate metal oxide–CNTs hybrids, supporting the catalysts on a suitable conductive support or embedding them within a carbon-matrix, makes it possible to overcome the problem of low electrical conductivity. For instance, Ni-Fe and Co-Mn layered double hydroxides supported on carbon

FULL PAPER

outperform precious-metal based systems such as IrO_2 or RuO_2 in catalyzing the OER.^[14,16] Moreover, supporting metal oxides on carbon materials can enable better distribution of the active component and prevent fast degradation.

In spite of the fact that numerous research works have revealed non-precious systems with impressive activities for either ORR or OER in alkaline media, it remains challenging to create viable and highly effective bifunctional oxygen electrodes able to reversibly catalyze both reactions over a long time during charge/discharge in batteries or cycling in URFC.[17] The benchmark catalysts widely used for oxygen electrochemistry (especially in acidic media) are still based on composites containing precious metal compounds, such as Pt/C, Pd/C, Ir/C, RuO₂ and IrO₂.^[17,18] However, these systems are known to be expensive and unstable, in particular, due to their high sensitivity to poisoning. Other approaches to develop the next-generation reversible oxygen electrodes involve the combination of non-precious single function ORR and OER catalysts into one hybrid system.^[19,20] For example, the introduction of ORR active M-Nx/C moieties into OER-evolving perovskites to form efficient bifunctional ORR/OER catalysts was previously demonstrated.[19] Another example involved direct growth of N-doped carbon nanostructures on the surface of OER-active compounds, such as perovskites and borides by chemical vapor deposition (CVD).^[21,22] The combination of ORR and OER catalysts into a composite aims at producing materials that can retain their individual properties or even slightly improve in performance owing to synergetic interaction. Moreover, several phase-pure compounds such as mixed oxides including perovskites and spinels have been reported to possess good bifunctional ORR/OER activity without additional manipulations and the use of carbon as a support or conductive additive.^[23,24] However, their deposition on a conductive support, or their embedment in such a support could lead to further improvement of the bifunctional ORR/OER activity.[24,25]

Most of bifunctional ORR/OER catalysts tend to suffer from relatively poor activity for one of the reactions leading to a low charge-discharge cycle efficiency, which manifests into a wide overvoltage between the OER and ORR, along with low stability.^[17] Intensive research is therefore aimed at identifying optimal bifunctional ORR/OER catalyst compositions along with better understanding of the factors influencing their performance to decrease the ORR/OER round trip overvoltage and improve the catalyst cyclability.

Herein, we present a simple strategy to produce mixed Fe-Co oxide nanoparticles supported on the surface of, or embedded inside oxidized multi-walled carbon nanotubes (Fe-Co/MWCNTs) as an effective bifunctional ORR/OER catalyst in alkaline electrolytes. By varying the Fe:Co ratio, we observed changes in phase composition, as well as the density and size of metal oxide nanoparticles embedded inside and on the surface of the MWCNTs resulting in a trend in the ORR and OER activity. This enabled identification of a Fe-Co/MWCNT catalyst composition with the highest bifunctional ORR/OER activity. Of the samples investigated, only mixed bimetallic oxides showed the most promising bifunctional ORR/OER activity. In particular, systems with an Fe:Co ratio close to 1:1 possessed the lowest ORR-OER round cycle overvoltage. Importantly, good electrocatalytic ORR activity and selective reduction of oxygen to OH- following the 4e pathway was achieved without functionalization of the catalyst and the support with nitrogen. The study therefore revealed that M-N_x-C moieties are not exclusively responsible and necessary for efficient ORR catalysis. In addition, the trend in the ORR/OER performance and its dependence on the particle size, composition and particle localization (inside or on the surface of the MWCNTs) further reveal intricacies of the interplay between structure, activity and stability of the catalysts. The optimized catalyst showed no evident loss in activity after 400 ORR/OER cycles at 15 mA cm⁻² in 6 M KOH thus demonstrating its potential for application in metal-air batteries or regenerative alkaline fuel cell technologies.

Results and Discussion

Investigations of morphology, structure, particle localization and chemical state of the Fe-Co/MWCNT catalysts

To obtain mono- or bimetallic (Fe-Co) oxide nanoparticles supported on oxidized multiwalled carbon nanotubes, with various Fe:Co ratios, the wet impregnation technique was used.^[26,27] The concentration of the initial iron and cobalt nitrate solution was varied to obtain samples with a total metal loading of ~ 13.5% wt. and different Fe:Co ratios. A batch of 13 samples with the general composition Fe_xCo_{1-x}/MWCNT with x = 1, 0.99, 0.95, 0.9, 0.7, 0.6, 0.5, 0.4, 0.3, 0.1, 0.05, 0.01, 0 was synthesized to study the dependence of the ORR/OER bifunctional activity on the catalyst composition.

Wet impregnation of carbon supports with a suitable metal oxide precursor followed by calcination is a simple and scalable method for preparation of carbon supported metal oxide particles. This method is however is not widely used due to complications of particle size control, low reproducibility, wide diameter distribution and surface agglomeration, among others.[28] This is partly attributed to low quality of the initial carbon nanotubes, for example, possessing wide diameter distribution, a high concentration of amorphous carbon and transition metal impurities. In our case, high quality MWCNTs grown on the bimetallic catalyst system by the improved Pechini route^[29,30,31] were first oxidized under controlled conditions.^[32] This helped to control the distribution of the microstructural defects and oxygen containing functional groups, e.g. carboxylic, carbonyl and hydroxyl groups, that enhance metal oxide particle adhesion and narrows their diameter distribution. The introduced functional groups serve as potential anchoring sites for Co and Fe cations on the surfaces of the MWCNTs. However, deviations in particle diameter distributions were still observable because the deposition takes place either on the surface of the MWCNTs, or inside the MWCNTs as revealed by HRTEM (Figure 1). Additionally, mild oxidation of the MWCNTs decreases their surface hydrophobicity and creates defects on the tube walls resulting in partial occupancy of the metal oxides inside the MWCNTs.

Since the tubes have a very high aspect ratio, large length-todiameter ratio, particle deposition cannot preferentially prevail via the tube ends. It is therefore expected that the deposition happens via the wall defects. This means the metal cations of the initial



Figure 1. HRTEM images and particle size histograms of Co, Fe and Fe-Co oxide particles supported on MWCNT with a total metal oxide loading of about 13.5 wt.%.

impregnation solution penetrate through the wall defects into the tube channels presumably by capillary forces.^[26]

Analysis of the HRTEM images (Figure 1 a-f) clearly reveals that for all the characterized samples, whether monometallic (Co or Fe) or mixed Fe-Co oxides, two ensembles of predominantly spherical nanoparticles of different average diameters localized inside and outside (on the surface) of the MWCNTs were formed. The particle size distribution of the metal oxides presented in Figure 1 (g-i) is based on evaluation of 200-300 particles for each sample. The metal oxide particles are distributed quite homogeneously within the carbon nanotube matrix especially for the bimetallic systems, however, their sizes and density of distribution, both inside the MWCNTs and on the surface of the MWCNTs, are dependent on the Fe:Co ratios of the final catalyst composition.

The number of nanoparticles located inside the MWCNTs was much higher for the cobalt-enriched samples with x = 0 to 0.4. For these samples, the proportion of the particles deposited on the surface of the MWCNTs was not higher than 24 %. Moreover, the average diameter of the particles on the surface of the MWCNTs for the Co-rich samples slightly increased, from 8-9 to 10-11 nm, with increasing Co concentration when x was decreased from 0.4 to 0.0, respectively. Deviation of the average diameters of the particles inside the MWCNTs was not that dramatic as their size is restricted by the channel width. A minimum particle diameter of 4 nm for the particles inside the MWCNTs was observed, for the samples with x = 0.3-0.4 while the largest particle size was 5.7 nm for the monometallic Co sample (x=0).

Although most of the analyzed samples possessed a quite narrow particle size distribution, deviations in particle diameter were still evident especially for the particles on the surface of the MWCNTs. The minimum particle sizes were similar for all of the analyzed samples, independent of the composition, typically, 1.7-1.8 nm and 2-2.8 nm for the particles inside and outside the MWCNTs, respectively. However, the sizes of the large particles varied more dramatically from 26 to 39 nm, for the outer and inner particles, respectively, when x was increased from 0.0 to 1.0.

The length of the particles inside the MWCNTs was in the range of 20-35 nm for all the studied samples. However, particles with such a high aspect ratio were seldom observed.

In general, samples with a Fe:Co ratio close to 1:1 yielded the smallest nanoparticles, both inside the MWCNT channels as well as on the surfaces. The proportion of the particles on the surface of the MWCNTs for cobalt-rich samples varied between 24 and 33% and increased with Fe concentration reaching 37% for x = 1. Moreover, the iron-rich samples exhibited more pronounced particle agglomeration on the surface of the carbon nanotubes in contrast to the bimetallic and Co-rich samples.

Further detailed phase analysis of the mixed oxide particles inside and on the surface of the MWCNTs were performed by additional HRTEM measurements on a setup with an integrated electron energy loss spectroscopy (EELS) analyzer, and by powder XRD. HRTEM of Fe_{0.4}Co_{0.6} and Fe_{0.5}Co_{0.5}, including dark field images, and EELS data are shown in Figure 2, clearly revealing the nanoparticles inside and outside of the MWCNTs. The HRTEM image of Fe_{0.4}Co_{0.6} shows lattice fringes of: 0.148±0.008 nm,



Figure 2. HR TEM images of (a) Fe_{0.4}Co_{0.6} and (b) Fe_{0.5}Co_{0.5} oxide particles inside a MWCNT channel. Dark field images c) and d) showing the particle distribution within the MWCNT matrix (inside the channel and on the surface), and EELS mapping of several Fe_{0.5}Co_{0.5} particles showing the distribution of Fe, Co and O.

 0.209 ± 0.008 nm, 0.241 ± 0.016 nm, 0.290 ± 0.008 nm assigned to the (440), (004), (113), (220) planes of the inverse spinel structure (227) of iron cobalt oxide or the (220), (200), (111) planes of CoO. Fringes of 0.349 ± 0.008 nm are also clearly visible and are assigned to the (002) planes of carbon, the distance between walls of MWCNTs.

The EELS data reveals that the particles attached on the surface of the MWCNTs walls are mainly mixed oxides of cobalt and iron with relative atomic concentrations of $62\pm 1\%$ (Co) and $38\pm 1\%$ (Fe) close to the nominal loading. Fine structure analysis of the L23 edges of Fe and Co shows the 3+ and 2+ oxidation states for Fe and Co, respectively, which is in agreement with the HRTEM data for the spinel structure of the oxide particles. The Fe L edge for the particles with 74% of iron showed a chemical shift of 1.5 eV, which corresponds to a transition to the Fe2+ oxidation state. The fine structure of the oxygen K edge corresponds to the Co2+ oxidation state. Noteworthy is that the small particles (2-5 nm) inside the MWCNTs are mostly pure CoO with no presence of Fe detected. This observation confirms dissimilarity of the phases of the particles inside the MWCNTs and those attached on their surface.

HRTEM data of $Fe_{0.5}Co_{0.5}$ show average lattice fringes of NPs: 0.209±0.008 nm, 0.241±0.016 nm, 0.290±0.008 nm, which are assigned to the (004), (113), (220) planes of the inverse spinel structure (227) of iron cobalt oxide. Fringes of 0.349±0.008 nm assigned to the (002) planes of carbon nanotubes are also clearly.

Analysis of EELS data for several particles attached on the surface of the MWCNTs (Figure 2 d) reveals the presence of both iron and cobalt with slightly different relative atomic concentrations. Most of the $Fe_{0.5}Co_{0.5}$ nanoparticles had a Fe/Co ratio of around 50/50, which is close to the nominal value. The oxidation states of Fe and Co were 3+ and 2+, which is characteristic of Fe and Co in a mixed Fe-Co spinel structure. Moreover, the oxidation states did not change with variation of the nanoparticle composition.

Powder X-ray diffraction (XRD) analysis (Figure 3) yielded crystalline sizes in good agreement with the HRTEM data. The 311 and 111 reflexes were chosen to analyze the distribution of the particle because of their high signal-to-noise ratio and negligible intensity of reflections from the MWCNTs. The (311) reflexes of Fe₃O₄, Fe_xCo_{3-x}O₄, Co₃O₄ and (111) of CoO, for some of the (Fe_xCo_{1-x}/MWCNT) samples, can be deconvoluted into two components corresponding to the two ensembles of the Fe-Co oxide particles of different sizes inside and outside the MWCNTs. The average diameters of the crystallites were determined using the Debye-Scherrer equation. In the case of the monometallic Febased sample, the presence of iron oxide with the spinel structure Fe₃O₄ phase was detected. The addition of cobalt up to a Fe:Co ratio of 1:1 (Fe_{0.5}Co_{0.5}) did not lead to significant changes in the diffraction patterns. Moreover, the crystallite sizes also remained essentially unchanged and were 3-4 nm and 10-11 nm, respectively, for the particles inside and on the surface of the

FULL PAPER



Figure 3. XRD patterns of Co_xFe_{1-x}/MWCNT samples with various Fe:Co ratios.

MWCNTs. Reflections related to the individual phases of cobalt oxide were not observed. The asymmetry of the peaks indicates defects in the Fe₃O₄ spinel structure ascribed to the formation of Co_xFe_{3-x}O₄ due to gradual replacement of iron by cobalt in the spinel structure.

The XRD patterns of Fe_{0.4}Co_{0.6} and Fe_{0.3}Co_{0.7} did not reveal any reflexes indicative of iron and cobalt compounds. The reflections at 25.0., 42.75 and 61.16° 20 arise from the MWCNTs. The XRD data thus confirms the presence of very small nanocrystallites. When the Co content was further increased, as in the case of $Fe_{0.1}Co_{0.9}$, $Fe_{0.05}Co_{0.95}$ and $Fe_{0.01}Co_{0.99}$, reflexes corresponding to the CoO phase became clearly pronounced in the XRD patterns. Only one ensemble of small nanocrystallites in the 6-8 nm size range were distinguishable when x was decreased from 0.1 to 0.01. In the case of the single-component Co-based sample, another cobalt oxide phase (Co₃O₄ with a spinel structure) was identified with two distinct particle sizes, 4 and 13 nm, corresponding to the particles inside the MWCNTs and on the surface of the MWCNTs. The results thus demonstrate a pronounced effect of the presence of Fe on the phase composition and the size of the nanocrystallites both inside and on the surface of the MWCNTs.

High resolution X-ray photoelectron spectroscopy (XPS) in the C 1s, O 1s, Co 2p and Fe 2p regions was employed to probe the chemical state of the catalyst surfaces, and the results are presented in Figure 4. The C 1s spectra are essentially invariant, indicating no evident change in the chemical state of carbon resulting from variation of the Fe:Co ratio. The O 1s region was deconvoluted for the pure Co and Fe samples. The peak at 535 eV can be assigned to water. The peaks at 531.5 and 533.2 eV are assigned to oxygen singly and doubly bound to carbon, respectively.^[33] The monometallic Co sample (Fe₀Co₁) shows peaks at 529.8 and 530.7 eV, assigned to hydroxide groups and lattice oxygen of Co₃O₄.^[34] Relatedly, the Fe₁Co₀ sample shows peaks at 530.2 and 531.6 eV assigned to hydroxide groups and lattice oxygen in Fe₂O_{3.^[34] respectively. As the peak position for} the hydroxide and lattice oxygen peaks exhibit only small deviations for iron and cobalt, it can be assumed that they are both present in the mixed phases. These peaks were not fitted for the mixed oxide samples for purposes of ease of visualization.

Due to strong multiplet separation, a detailed deconvolution of XP spectra of first row transition metals is demanding. The Co 2p high-resolution spectra are of low intensity, due to the low Co loading. The Co 2p spectra show the Co 2p_{1/2} and Co 2p_{3/2} peaks at 795.8 and 780.4eV. The Co 2p region for the Fe₀Co₁ samples is characteristic of Co₃O₄ as the peak shape is very similar to literature reported spectra for Co₃O₄.^[35] We infer that Co₃O₄ is also present in the mixed oxide samples, as the spectra look very similar to that of the pure Co sample. It is important to keep in mind that the Co 2p region overlaps with the Fe LMM Auger signal at 786 eV, which ought not to be misinterpreted as satellite feature. The Fe 2p high-resolution spectra are of low intensity, due to the low Fe loading. The Fe 2p spectra show the Fe 2p_{1/2} and Fe 2p_{3/2} peaks at 724.2 eV and 710.8 eV. The Fe 2p region for the Fe₁Co₀ sample suggests that Fe is present in the 3+ oxidation state due to the absence of intensive shake up satellite peaks.^[36] it should however be noted that the Fe 2p region overlaps with the Co LMM Auger signal at 715 eV, which should therefore not be interpreted as a satellite feature.

From the data presented above, it is concluded that altering the Fe:Co ratio in the Fe_xCo_{1-x}/MWCNT catalyst leads to the formation of different mono- or bimetallic oxide phases with various crystalline sizes and particle density, inside and on the surface of the MWCNTs. The changes in particle diameter, distribution, degree of agglomeration of the particles on the surface of the MWCNTs, and preferential formation of small Co enriched particles inside the MWCNTs can be partly explained on the premise of the initial pH of the cobalt and iron nitrate solutions and their mixtures, as well as the different ion interactions during the drying step. Additionally, the defects in the walls of the MWCNTs created during the oxidation step are expected to facilitate penetration of metal cations into the core of the MWCNTs. Solvated cobalt cations, which possess a smaller ionic radius compared to solvated iron cations, obviously penetrate into the channels of the MWCNTs more easily through the wall defects to give rise to preferential Co enrichment of the nanoparticles inside the MWCNTs as observed by HRTEM.

Bifunctional ORR/OER activity of the Fe_xCo_{1-x}/MWCNT catalysts

To evaluate the bifunctional electrocatalytic activity of the prepared Fe_xCo_{1-x}/MWCNT samples toward the ORR and the OER, linear sweep voltammograms were recorded in oxygen saturated 0.1 M KOH at a scan rate of 5 mV s⁻¹ and electrode rotation at 1600 rpm, in a potential window covering both ORR and OER. Results of the electrochemical characterization of the various Fe_xCo_{1-x}/MWCNT catalysts with various Fe:Co ratios are presented in Figure 5, and the important ORR, OER and bifunctional (ΔE (V) = E_{OER}-E_{ORR}) electrocatalytic parameters are summarized in table 1. Figure 5a shows a qualitative depiction of the influence of the Fe:Co ratio on the performance of the catalysts. Although the unmodified MWCNTs also display some activity for both ORR and OER, their modification with either the monometallic (Co or Fe) oxides or the bimetallic (Co and Fe) mixed oxides lead to considerable enhancement of both the ORR and the OER. The potentials presented in table 1 for both OER and ORR were obtained from 4 independent measurements. The bifunctional parameter ∆E (V) for all of the Fe_xCo_{1-x}/MWCNT catalysts developed here, expressed as the difference in the potential of the ORR at a current density of -1 mA cm⁻² and the

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Figure 4. High resolution XPS spectra of the C 1s, O 1s, Co 2p and Fe 2p regions, of CoxFe1. //MWCNT samples with various Fe:Co ratios.

OER at a current density of +10 mA cm⁻², is plotted versus again the Fe content (x) in the samples. Figure 5c therefore shows a trend of the bifunctional activity when the concentration of iron is gradually increased (Figure 5c). The results revealed that increasing the Fe content initially leads to improvement of the bifunctional activity until the Fe:Co ratio reaches 1:1, after which, further increase of the Fe:Co ratio led to a decline of bifunctional ORR/OER activity for all the Fe-rich samples. Importantly, it was observed that the Fe_xCo_{1-x}/MWCNT samples with x \approx 0.5 exhibited the lowest bifunctional parameter with the monometallic oxide catalysts (Fe or Co) showing the worst performance as bifunctional catalysts, and for the individual ORR and OER reactions.

Importantly, when the ORR and OER activities, as potentials E(V) at -1 mA cm⁻² and 10 mA cm⁻², respectively, of the Fe_xCo_{1-x}/MWCNT samples with various Fe:Co ratios are separately plotted against the Fe content (x), slightly different activity trends are observed (Figure 5 d). Fe_{0.4}Co_{0.6}/MWCNT exhibited the best OER activity, affording a current density of 10 mA cm⁻² at 1.613 V (versus RHE). This catalyst also exhibited the best bifunctional ORR/OER activity although its ORR activity, 0.782 V at -1.0 mA cm⁻² was slightly lower than that for Fe_{0.5}Co_{0.5}/MWCNT, which had 0.789 V at the same current density.

Of the metal oxide catalysts, the monometallic catalyst, Fe_{1.0}/MWCNT had the worst OER activity with 1.727 V at 10 mA cm^{-2} . Increasing the Co concentration led to enhancement of the

OER activity up to a Fe:Co ratio of 0.4:0.6 (2:3), or x =0.4. When the proportion of Co was increased beyond this value (2:3), in other words, for x <0.4, the OER activity declined gradually, reaching 1.651 V for the cobalt only catalyst $Co_{1.0}$ /MWCNT. Beginning with the pure Fe only catalyst (x =1), the ORR improved with decrease of x from 1.0 to 0.5, with an inverse trend arising thereafter. Increasing the proportion of Co above 0.6 (x <0.4) led to increase of the bifunctional parameter, resulting from increase of the overpotentials for both reactions. For these samples (x <0.4), the relative difference in the ORR potential in relation to the sample with x =0.4 (Fe_{0.4}Co_{0.6}/MWCNT) was not higher than 2-4 mV, however, the relative increase in the OER potential reached 38 mV for the x =0, for the Co only catalyst.

When we compare the Fe_xCo_{1-x}/MWCNT samples with Fe content higher than 50 at. % (x =0.5), the differences of the bifunctional parameter increased much faster with increase of the Fe concentration in contrast to the Co-rich samples (Table 1). As was discussed earlier, the Fe-rich samples possessed higher particle sizes, with a higher degree of particle of particle agglomeration on the surfaces of the MWCNTs. These factors lead to a decrease of the surface area leading to the observed decline of the bifunctional ORR/OER activity. Moreover, the electrocatalytic activity is influenced by strong phase separation, with Fe₃O₄



Figure 5. a) polarization curves (iR compensated) of Fe_xCo_{1-x}/MWCNT samples with various Fe:Co ratios; b) hydrogen peroxide yield calculated from the RRDE experimental curves; c) dependence of the bifunctional parameter ΔE (V) on the Fe:Co; d) dependence of the ORR and OER activities (obtained at -1 and +10 mA cm⁻², respectively). Data obtained in O₂ - saturated 0.1 M KOH at a scan rate of 5 mV s⁻¹ and at 1600 rpm electrode rotation speed.

particles dominating on the surface of the MWCNTs (for x =0.7 and higher) as revealed by XRD and HRTEM analysis. The decrease of the bifunctional parameter is mostly caused by decline in the OER activity. The ORR activity only dropped marginally. FeOx based materials are typically poorer OER catalysts in contrast to CoOx-based materials, independent of particle size effect and nature of the support.^[17,24] It was previously reported that the OER activity decreases in the order of NiO_x > CoO_x > FeO_x > MnO_x,^[14,37] determined by the strength of bonding of the transition metal and OH. However, the M-O bond strength as well as active site density can be tuned by the rational combination of several transition metals.[38] The origin of enhanced ORR and OER activity for the mixed-oxide samples can not only be explained in terms of synergistic interaction but also arise due to improvement in the conductivity of catalytic films, particularly for the cobalt rich samples.^[7,8,24] Moreover, particle size also influences strongly on the electrocatalytic activity of transition metal oxides.^[39] Seo et al. ^[39] observed a dramatic influence of the size of cobalt oxide nanoparticle supported on carbon nanotubes on their OER performance, however, the ORR activity remained almost unchanged when the particle size was increased from 4 to 10 nm.

In order to investigate the selectivity of oxygen reduction on the various Fe_xCo_{1-x}/MWCNT catalysts, RRDE measurements were conducted at a scan rate of 5 mV s⁻¹ and rotation speed of 1600 rpm. The collection efficiency (N) for calculation of the hydrogen peroxide yield was determined for each electrocatalytic film separately. The data on the hydrogen peroxide formation (Figure 4 b) indicate that the electrocatalysts with the lowest H₂O₂ yield are those that contained mixed Fe-Co oxides. The introduction of Fe to the tune of 10-30% significantly increased the catalyst selectivity via the 4-electron transfer pathway to form OH⁻ in contrast to monometallic Co catalysts. The lowest peroxide yield (less than 2.5%) was obtained for the catalyst with an Fe:Co ratio of 3:7 (Fe_{0.3}Co_{0.7}). Further increase of the iron content above the Fe:Co ratio of 3:7 led to more intensive hydrogen peroxide formation. Sample with Fe_{0.4}Co_{0.6} and Fe_{0.5}Co_{0.5} showed a maxim H_2O_2 yield of 5-7%. Iron-rich (Fe_{0.7}Co_{0.3} and Fe_{0.9}Co_{0.1}), as well as pure Fe- catalysts produced much more pronounced yields of hydrogen peroxide. Several works have shown that monometallic oxides dispersed on carbon supports produce more

FULL PAPER

Table 1. Electrochemical results of the ORR, OER and bifunctional ORR/OER activity of conducted in 0.1 M KOH at 1600 rpm. Data are the mean values of 4 independent experiments, error is \pm 3mV. The lowest overpotentials for the OER, the ORR, and bifunctional ORR/OER are marked in red.

Sample	E ORR at -1 mA cm ⁻² , V	E OER at +10 mA cm ⁻² , V	ΔΕ, V
Fe ₀ Co ₁	0.778	1.651	0.873
Fe _{0.01} Co _{0.99}	0.780	1.641	0.861
Fe _{0.05} Co _{0.95}	0.779	1.629	0.850
Fe _{0.1} Co _{0.9}	0.772	1.623	0.851
Fe _{0.3} Co _{0.7}	0.777	1.615	0.838
$Fe_{0.4}Co_{0.6}$	0.782	1.613	0.831
Fe _{0.5} Co _{0.5}	0.789	1.625	0.836
Fe _{0.6} Co _{0.4}	0.785	1.627	0.842
Fe _{0.7} Co _{0.3}	0.764	1.635	0.871
Fe _{0.9} Co _{0.1}	0.734	1.664	0.930
$Fe_{0.95}Co_{0.05}$	0.727	1.694	0.967
Fe _{0.99} Co _{0.01}	0.717	1.703	0.986
Fe ₁ Co ₀	0.719	1.727	1.008
ox-MWCNTs	0.710	1.784	1.077

hydrogen peroxide than Co rich samples, and that Fe₃O₄/C can be an effective catalyst for hydrogen peroxide formation.^[40] However, doping carbon supports with nitrogen significantly improves the ORR selectivity of monometallic Fe and Co catalysts via the 4-electron transfer pathway to form OH^{-.[10,47]} In our case, nitrogen-free Fe_xCo_{1-x}/MWCNT samples revealed high 4-electron ORR selectivity, which can be attributed to a synergetic between Fe and Co, as well as optimal active site distribution. Moreover, it is known that oxidized carbon nanotubes can also have some reasonable activity for ORR due to the presence of oxygen functionalities, particularly, quinone groups, at the surface and at defect edges.^[41] However, the pure oxidized carbon nanotubes

Bifunctional durability of Fe-Co/MWCNTs in 6 M KOH solution

Fe0.4Co0.6/MWCNT being the most active sample with the lowest overvoltage difference between OER and ORR was chosen for durability investigation during charge-discharge cycling under harsh alkaline conditions. The catalyst powder was immobilized on a gas diffusion electrode by a spray coating technique and galvanostatically charged and discharged at ±15 mA cm⁻² in a 3electode cell in a 6 M KOH solution as described in.[22] The OER and ORR potentials versus number of charge-discharge cycles are presented in Figure 6. The OER potential remained unchanged after 400 charge/discharge cycles, meanwhile, the ORR potential decreased only marginally, by 0.04 V from the first to second cycle (Figure 6 left) indicating decline in the ORR activity after subjecting it to the anodic OER conditions. However, after the first charge/discharge cycle, the ORR and OER potentials remained constant for the rest of the stability test, indicating that the electrocatalytic Fe-Co/MWCNT systems developed here retain their activity when repeatedly switched from OER to ORR conditions and back. These results confirm outstanding bifunctional stability of the Fe-Co electrocatalyst in the course of 400 alternating cycles of ORR and OER polarization at a current density of ±15 mA cm⁻² in a highly concentrated alkaline electrolyte. One of the possible reasons for the high catalytic stability could be the localization of the most Fe-Co oxide nanoparticles (≥76%) inside the MWCNTs, which shield them from fast dissolution during the cycling. This conclusion is supported by previous studies where spinel Co-Mn oxide nanoparticles partially embedded in MWCNTs exhibited exceptional stability as bifunctional ORR/OER catalysts, which was attributed to encapsulation of the metal oxide particles inside the MWCNTs.^[42] In related studies, durable electrocatalysis of O₂ reduction has been achieved by Fe nanoparticles embedded inside MWCNTs.^[43] The graphitic walls of the MWCNTs thus prevent the embedded particles from rapid dissolution by preventing their direct contact with the electrolyte.



Figure 6. Potential versus number of charge/discharge cycles recorded at ±15 mA cm⁻²of a gas diffusion layer modified with Fe_{0.4}Co_{0.6}/MWCNT by spray coating.

FULL PAPER

Conclusions

A simple procedure for designing bifunctional oxygen evolution/oxygen reduction electrocatalysts based on mixed Fe-Co oxide nanoparticles supported on/or embedded inside oxidized multiwalled carbon nanotubes is developed. A clear composition dependent trend in bifunctional activity was demonstrated for various Fe:Co ratios. Among the prepared Fe_xCo_{1-x}/MWCNT samples of various Fe:Co ratios, samples with Fe:Co ratio close to 1 demonstrated the lowest overpotentials between the ORR and the OER, as well as a high selectivity for preferential reduction of oxygen to OH⁻ during the ORR. The improvement of the bifunctional activity for the mixed oxide nanoparticles can be ascribed to a synergetic effect, as well as film conductivity and active site density of the bimetallic systems. Moreover, the size and localization of the nanoparticles, both inside and on the surface of the MWCNTs varied with the Fe:Co ratio, and influenced the catalytic performance. Importantly, high bifunctional ORR/OER activity, and ORR selectivity towards the 4-electron reduction of O_2 to OH^- were achieved without functionalization of the catalyst with nitrogen, thus unveiling a design approach for an efficient noble metal-free catalysts for electrocatalysts. Additionally, the optimized catalyst sustained at least 400 charge-discharge cycles at 15 mA cm⁻² in 6 M KOH, within any visible loss in performance, which makes the catalyst very promising for reversible oxygen electrodes with potential application in metal-air batteries among others.

Experimental Section

Synthesis and functionalization of MWCNTs

MWCNTs of average diameters 8-10 nm were synthesized by the chemical vapor deposition (CVD) technique based on ethylene decomposition over bimetallic Fe-Co catalysts at 680 °C. The multicomponent catalysts were prepared by optimized Pechini technique that allowed a narrow tube diameter distribution to be achieved.^[30,31] Carbon nanotubes were further mildly oxidized in concentrated nitric acid for 120 min under continuous stirring with subsequent washing in pure distilled water and drying in air (hereafter denoted as MWCNT). HRTEM images of the oxidized carbon nanotubes prior to deposition of the metal oxides are presented in Figure S1. The introduction of oxygen groups during this treatment has been evaluated by DTA/TGA as described in detail in.^[32] This treatment resulted in the formation of about 2.4 carboxylic groups per 1 nm⁻² with almost no drop in the surface area after the oxidative treatment (300 m²/g). The purity of the final oxidized MWCNT was higher than 99%, and the main impurities are the catalyst particles inside the tube core. No amorphous carbon was observed.

Preparation of Co, Fe and Co-Fe/MWCNT electrocatalysts

Co, Fe and Co-Fe-oxide/MWCNT samples were prepared by incipient wet impregnation of oxidized MWCNTs with aqueous solutions of cobalt (II) and iron (III) nitrates.^[26,27] After impregnation for 12 h, the products were dried at 110 °C for 4 hours followed by calcination at 350 °C for 4 hours under an argon atmosphere. By varying the concentrations of cobalt and iron in the cobalt-iron nitrate solutions, samples with different catalyst loadings and Fe:Co ratios were obtained. Preliminary tests showed that samples with 13.5 wt % total metal content are the most promising catalysts and were thus chosen for further detailed characterization and electrochemical tests.

The prepared samples are denoted as $n\% \text{ Fe}_x\text{Co}_{1-x}/\text{MWCNT}$, where n is the total metal loading (wt. %) and varied from 13.4 to 13.6 wt %, x and 1-x are the atomic concentration of Fe and Co, respectively. For this work, a batch of 13 samples with x equal to 1, 0.99, 0.95, 0.9, 0.7, 0.6, 0.5, 0.4, 0.3, 0.1, 0.05, 0.01, 0 was synthesized and used for the physical-chemical characterizations and electrochemical studies.

Structural characterization

Powder XRD measurements were carried out using an ARL X'TRA diffractometer (Thermo Electron Corporation, Switzerland) equipped with the vertical theta geometry (Bragg-Brentano), Cu K- α radiation (λ =0.15418 nm) and a Peltier cooled Si (Li) solid-state detector. The scanned 20 range was from 20° to 85° in steps of 0.05° and a counting time of 3 s. Phase analysis was performed using the ICDD PDF-2 database. Phase composition analysis was performed using the Rietveld method in the Topas program.

XPS measurements were carried out in an ultra-high vacuum set-up (UHV) equipped with a high resolution Gammadata-Scienta SES 2002 analyzer. A monochromatic AI K α X-ray source (1486.3 eV; anode operating at 14.5 eV and 30.5 mA) was used as incident radiation and a pass energy of 200 eV was chosen resulting in an energy resolution better than 0.5 eV. Charging effects were compensated using a flood gun. Binding energies were calibrated by positioning the main C 1s peak at 284.5 eV.

The microcrystallinity of the Co, Fe and Co-Fe/MWCNT samples was characterized using a JEOL JEM-2010 microscope operating at 200 kV accelerating voltage which allows a nominal resolution of 1.4 Å to be achieved. Sample suspensions for TEM studies were prepared by dispersion of the powder in hexane in a glove box under an argon atmosphere. The hexane suspension was removed from the box and a drop cast onto a micro-mesh copper grid and then quickly transferred to the TEM vacuum chamber where it evaporated. The total time of exposure of the hexane suspension to the atmosphere was 20 s. The mean diameter of the MWCNTs and Fe-Co particle size distribution were estimated from a statistical count of the nanotubes from several frames taken on different parts of the samples. The average diameter distribution of tubes as well as particle distribution were controlled by statistical analysis of 200-300 tubes using the Gatan Micrograph software package.

More detailed TEM characterization was performed using a Titan 80-300 microscope (operated at 80 kV) and equipped with image Cs corrector and monochromator for high energy resolution in Electron Energy Loss Spectroscopy (EELS) studies. EELS measurements were carried out in the STEM mode on a Gatan Quantum GIF spectrometer. The TEM samples were prepared by dispersing the nanotubes in acetone and then casting them onto a copper grid coated with a lacy carbon film.

The morphology of the metal-oxide/MWCNT powders was investigated by the FIB/SEM with FEI Helios Nanolab dual beam. The microscope is fitted with an X-max 80 mm² EDS detector from Oxford Instruments. The accelerating voltage of 20 kV was chosen for the full set of X-ray lines being efficiently excited and to optimize the EDS acquisition parameters. During the EDS map acquisition, drift is compensated every 2 min by cross-correlation of the electron beam (SE) images. The SE images were obtained using the ICE detector outside the electron column.

Electrochemical characterization

Co, Fe and Fe-Co/MWCNT-containing inks were prepared separately to a concentration of 5 mg ml⁻¹. A mixture of ultrapure water, ethanol and Nafion solution (5 wt%, Sigma Aldrich) in the volume ratio 49:49:2 was used as dispersion solvent. The mixtures were then sonicated for at least 30 min to obtain a well-dispersed catalyst ink suspension.

FULL PAPER

Glassy carbon electrodes (3.8 mm and 5.0 mm diameter) were used as rotating disk electrodes (RDEs) and rotating ring-disk electrodes (RRDEs), respectively. RDEs were polished with 1.0 and 0.3 µm alumina pastes prior to each measurement. Catalyst inks (4.8 and 8.3 µL) were cast onto the RDEs and RRDEs, respectively, and air dried to obtain a catalyst layer with a loading of 210 mg cm⁻². The RRDE data was used to calculate the hydrogen peroxide yield dependent on the potential for the oxygen reduction reaction.

The air electrode for the long-term stability measurement in a 6 M KOH solution was prepared by spray-coating the catalyst onto a carbon cloth gas diffusion layer (MTI) to reach a loading of about 1.0 mg cm⁻² (geometric surface area). The ink for the spray coating was prepared similarly as for the RDE measurements, however no water was used (98:2 ethanol:Nafion volumetric ratio).

All measurements were performed with an AutolabIII/FRA2 potentiostat/galvanostat (Metrohm) attached to a RDE 710 rotator (Gamry Instruments). The standard experiments were conducted in a threeelectrode coaxial cell configuration in 0.1 M KOH at 1600 rpm. The electrolyte was saturated with oxygen and an oxygen stream was kept above the solution during all the measurements. A cylindrical-shaped Pt mesh was used as the counter electrode (CE) and Ag/AgCl/KCl (3 M) was used as the reference electrode (RE). The coaxial cell geometry, in which the working electrode is surrounded by the CE and the RE is placed outside the CE, creates a symmetrical distribution of the current lines and, thus, diminishes the influence of the electrode position on the determination of solution resistance, thereby leading to more precise determination of the ohmic drop.^[11] All potentials were later converted to the reversible hydrogen electrode scale (RHE), according to Equation (1):

 $\mathsf{E}_{\mathsf{RHE}} = E_{Ag/AgCl} + 0.059 \, \mathrm{pH} + E_{\mathsf{Ag/AgCl}}^{\circ}$

The pH value was corrected taking into account the activity coefficient of 0.1 M KOH.

EIS measurements were performed before each experiment at the opencircuit potential between 10 kHz and 200 Hz with a 10 mV AC amplitude. The electrolyte resistance was extracted from the real impedance of Nyquist plots at high frequency, and was used for ohmic drop (iR) correction of the data. This was followed by a conditioning step that involved running continuous voltammograms from 0.1 to -0.5 V versus Aq/AqCl/KCl (3 M) at 100 mV s⁻¹ until reproducible voltammograms were obtained. Finally, linear-sweep voltammograms were recorded between 0.1 and -1 V and 0.1 and +1 V versus Ag/AgCI/KCI (3 M) at 5 mV s⁻¹ one after another, in order to observe the electrocatalytic properties of the materials in the ORR and OER regions. A rotation speed of 1600 rpm was used to avoid accumulation of evolved oxygen bubbles on the surface of the electrode in the case of OER measurements. A bifunctionality parameter AEOER-ORR was determined by subtracting the potential (iR corrected) corresponding to a current density of +10 mA cm⁻² during the OER from that corresponding to a current density of -1 mA cm⁻² during the ORR, as derived from the LSVs. In the RRDE experiments, the ring potential was set to 0.4 V versus Ag/AgCl/ KCl (3 M) meanwhile the potential at the disk was scanned from 0.V to -1.0 V versus Ag/AgCI/KCI (3 M) to record the ORR current. The selectivity was evaluated from the RRDE data according to Equation (2):

 $H_2O_2(\%) = 200 * \frac{I_{R/N}}{I_{R/N} + I_D}$

where I_D and I_R are the disk and ring currents, respectively, and N is the collection efficiency determined by using the RRDE measurements for each sample in 5 mm potassium ferrocyanide solution.^[12]

To evaluate the long-term stability of the samples at conditions close to real application, for instance, in alkaline Zn-air batteries, alternate ORR/OER polarization curves were recorded in 6.0 M KOH in a homebuild 3-electrode cell.^[22] The 6 M KOH solution was continuously saturated with oxygen during the measurements. A commercial Hg/Hg₂Cl₂/KCl (sat) was used as a reference and Ni(OH)₂ was used as a counter electrode. The last was chosen to ensure that the stability measurements are not limited by the cyclability of the counter electrode as well as side products such as hydrogen gas are not produced during the measurements. The galvanostatic charge-discharge tests were conducted at 15 mA cm⁻² with 10 minutes for each cycle. The potentials are referred to the Zn/Zn(OH)42 (6 M KOH) to facilitate the interpretation of the air-electrode performance. In order to reference the potential to Zn/Zn(OH)₄²⁻ (6 M KOH), the OCP of zinc metal was determined under similar conditions in an independent experiment using Ni(OH)₂ as counter and reference electrode. The obtained value was 1.54 V, which allowed us to convert the potential measured in the 3-electrode cell to the Zn/Zn(OH) 42- (6 M KOH) scale.

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FULL PAPER

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A facile strategy to produce efficient bifunctional ORR/OER catalysts comprised of mixed Fe-Co nanoparticles supported on/and embedded inside oxidized multiwalled carbon nanotubes was developed. The optimized catalyst with Fe:Co ratio of 2:3 afforded a low OER/OER reversible overvoltage of only 0.83 V, and exhibited very promising long-term stability with no evident change in the potential for both the ORR and the OER after 400 charge/discharge (OER/ORR) cycles at 15 mA cm⁻² in 6 M KOH.



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Page No. – Page No.

Bifunctional oxygen reduction/oxygen evolution activity of mixed Fe-Co oxide nanoparticles with variable Fe:Co ratios supported on multiwalled carbon nanotubes