Mesoporous MnCo$_2$O$_4$, NiCo$_2$O$_4$, and ZnCo$_2$O$_4$ Thin-Film Electrodes as Electrocatalysts for the Oxygen Evolution Reaction in Alkaline Solutions

Assel Amirzhanova, Nesibe Akmaşen, Irmak Karakaya, and Ömer Dag*

ABSTRACT: The oxygen evolution reaction (OER) is the bottleneck of the electrochemical water-splitting process, where the use of porous metal oxide electrodes is beneficial. In this work, we introduce a one-pot synthesis method to fabricate a series of mesoporous metal cobaltite (m-MCo$_2$O$_4$, M = Mn, Ni, and Zn) electrodes for the OER. The method involves preparation and coating of a homogeneous clear solution of all ingredients (metal salts and surfactants) over a fluoride-doped tin oxide surface as a thin lyotropic liquid crystalline film and calcination (as low as 250 °C) to obtain a 400 nm thick crystalline m-MCo$_2$O$_4$ electrode with a spinel structure. Mesophases and m-MCo$_2$O$_4$ films are characterized using structural and electrochemical techniques. All electrodes are stable during the electrochemical test in 1 M KOH aqueous solution and perform at as low as 204 mV overpotential at 1 mA/cm$^2$ current density; the m-NiCo$_2$O$_4$ electrode works at current densities of 1, 10, and 100 mA/cm$^2$ at 227, 300, and 383 mV overpotentials after compensating the IR drop, respectively. The Tafel slope is 60 mV/dec for the m-NiCo$_2$O$_4$ and m-ZnCo$_2$O$_4$ electrodes, but it gradually increases to 85 mV/dec in the m-MnCo$_2$O$_4$ electrode by thermal treatment, indicating a change in the OER mechanism.

KEYWORDS: molten salt-assisted self-assembly, metal cobaltites, mesoporous materials, electrocatalysis, oxygen evolution reaction

INTRODUCTION

Mesoporous and nanoscaled metal oxides, metal sulfides, carbon, metal–organic frameworks, and phosphates are important materials in the production and storage of clean energy.\textsuperscript{1-11} Especially, mesoporous spinel oxides have been widely investigated for water oxidation electrocatalysis.\textsuperscript{14-22} Transition-metal cobaltites (MCo$_2$O$_4$) are employed as efficient electrocatalysts for water oxidation and as electrodes in supercapacitors and batteries;\textsuperscript{17-22} therefore, many strategies have been developed to synthesize these materials.\textsuperscript{23,24} Most methods produce powder samples that require further fabrication steps and special chemicals to build into electrodes. Designing synthetic strategies that involve one-pot, single-step film fabrication would help to enable the development of these electrodes for practical use. Manganese, nickel, and zinc cobaltites have special significance due to the abundance of Mn, Ni, and Zn in the earth’s crust, and they are used as stable electrodes in many applications. For instance, mesoporous MnCo$_2$O$_4$ has been successfully employed for both the oxygen evolution reaction (OER) and oxygen reduction reaction.\textsuperscript{17} NiCo$_2$O$_4$ displays good OER performance at relatively low overpotential values\textsuperscript{18} and is a good candidate for supercapacitors.\textsuperscript{19} Similarly, ZnCo$_2$O$_4$ displays high electrochemical activity/stability in energy-storage applications as a capacitor\textsuperscript{20} and lithium–oxygen batteries in addition to the OER-active electrode material.\textsuperscript{21,22}

Several methods have been developed to synthesize mesoporous transition-metal oxides and mixed oxides. These methods can be divided into two main categories; hard and soft templating.\textsuperscript{25-39} Hard-templating methods produce ordered mesoporous powders but require multiple tedious steps.\textsuperscript{25-29} Soft-templating methods involve surfactants and self-assembly processes in both the solution phase\textsuperscript{30-32} and lyotropic liquid crystalline mesophase (LLCM).\textsuperscript{33-39} Solution-phase synthesis is less successful and produces powders; however, LLCM-mediated synthesis is quite successful in producing metal oxides as thin films and monoliths.\textsuperscript{33-39} LLCM-mediated synthesis can be employed by either using a polymerizing agent [such as tetramethyloxysilicate, Si(OCH$_3$)$_4$, or titanium tetrabutoxide, Ti(OC$_3$H$_7$)$_4$] and a transition-metal salt\textsuperscript{33-35} or directly using only transition-metal salts.\textsuperscript{6-39} The formation of a salt...
surfactant LLCMs was introduced nearly 20 years ago. Simply, the LLCMs, where the molten salt behaves as a solvent. The salt species are in the molten phase in the hydrophilic domains of mesophases and thin pores in favor of large ones. Therefore, the resulting structures and surfactant during calcination and/or collapse of the small pores due to the evolution of gaseous products of salt species, water, due to surfactant domains in the LLCM and the large pores form porous materials have two pore systems; the small pores form films or monoliths upon calcination over 300 °C. The resulting porous materials have two pore systems; the small pores form due to surfactant domains in the LLCM and the large pores form due to the evolution of gaseous products of salt species, water, and surfactant during calcination and/or collapse of the small pores in favor of large ones. Therefore, the resulting structures have ideal pore systems and are beneficial in catalytic applications. The MASA method has already been used to produce electrodes for the OER, such as LiCoO$_2$, LiMn$_2$O$_4$, and NiO as thin-film electrodes. Thin films have uniform two-pore systems which make them highly active as electrocatalysts for the OER. The lithium and metal salts and two transition-metal salts synergistically affect each other in the mesophase, each enhancing the solubility of the other, lowering their melting points, and hindering the crystallization of the salt species to stabilize the LLCMs. This work (as outlined in Scheme 1) is the first example of the use of two transition-metal salts without lithium salt in the mesophase. We investigate Mn(II)/Co(II), and Zn(II)/Co(II) salt couples as examples of different total salt [M(II) plus Co(II)] to surfactant mole ratios, from 6 to 25. All metal salts are aqua complexes of nitrate salts ([M(H$_2$O)$_n$(NO$_3$)$_x$]). The nickel (or manganese) to cobalt salt mole ratio was kept as 1:2 to make sure that the calcination product is a pure spinel structure of MCo$_2$O$_4$. The concentrations of cetyl trimethyl ammonium bromide (CTAB) and C$_{12}$H$_{25}$(OCH$_2$CH$_2$)$_{20}$OH (C$_2$E$_{10}$) were kept constant at 1:1 mole ratio in all solutions and were used at amounts of 0.291 and 0.500 g, respectively. Ethanol was used as a primary solvent to homogenize the mixtures. Higher salt ratios required more ethanol to obtain clear solutions. Thus, from 6 to 12 salt to surfactant mole ratios, the amount of ethanol used to homogenize the mixtures was 5 mL and from 15 to 25 salt to surfactant mole ratios, 10 mL of ethanol was used.

A typical solution preparation is as follows: for example, the 6 mole ratio of nickel solution, first 0.464 g of [Ni(H$_2$O)$_6$](NO$_3$)$_2$, 0.929 g of [Co(H$_2$O)$_6$](NO$_3$)$_2$, 2.01 g of C$_{12}$H$_{25}$(N(CH$_3$)$_3$)Br (CTAB), and 5 mL of ethanol were added into a vial and stirred for 15 min using a magnetic stirrer to obtain a clear solution. Then, 0.500 g of a non-ionic surfactant (C$_2$E$_{10}$) was added to the clear solution and stirred for another 30 min to obtain a final clear and homogeneous solution. Accordingly, the amount of Ni(II) and Co(II) added was changed; for the other solutions, see Table S1. The same procedure was used to prepare all other solutions.

For Zn(II)/Co(II) solutions, P123 [H−(OCH$_2$CH$_2$)$_{20}$−(OCH$_2$CH$_2$)$_{20}$OH] has been used with a slight modification of the above procedure. For preparing a 20:40:5:1 (Zn(II):Co(II):CTAB:P123) solution: 1.0 g of P123 was added to 5.0 mL of deionized water in a 25 mL glass vial and the mixture was stirred with a magnetic stirrer overnight to obtain a clear solution. Then, 0.314 g of CTAB was added to the clear solution and stirred until it became clear. Finally, 1.024 g of [Zn(H$_2$O)$_6$](NO$_3$)$_2$ and 2.000 g of [Co(H$_2$O)$_6$](NO$_3$)$_2$ were added to the above solution and the solution was stirred until a clear red solution was obtained. The compositions of all solutions are given in Table S1.

**Scheme 1. Outline of the Work**

**EXPERIMENTAL PART**

**Preparation of M(II)/Co(II) Solutions.** M(II)/Co(II) (M is Ni and Mn) solutions were prepared at different total salt [M(II) plus Co(II)] to surfactant mole ratios, from 6 to 25. All metal salts are aqua complexes of nitrate salts ([M(H$_2$O)$_n$(NO$_3$)$_x$]). The nickel (or manganese) to cobalt salt mole ratio was kept as 1:2 to make sure that the calcination product is a pure spinel structure of MCo$_2$O$_4$. The concentrations of cetyl trimethyl ammonium bromide (CTAB) and C$_{12}$H$_{25}$(OCH$_2$CH$_2$)$_{20}$OH (C$_2$E$_{10}$) were kept constant at 1:1 mole ratio in all solutions and were used at amounts of 0.291 and 0.500 g, respectively. Ethanol was used as a primary solvent to homogenize the mixtures. Higher salt ratios required more ethanol to obtain clear solutions. Thus, from 6 to 12 salt to surfactant mole ratios, the amount of ethanol used to homogenize the mixtures was 5 mL and from 15 to 25 salt to surfactant mole ratios, 10 mL of ethanol was used.

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**Synthesis of Mesoporous MCo$_2$O$_4$ (M = Ni, Mn, and Zn) Thin Films and Monoliths.** Clear solutions were spread on glass slides via either spin-coating (for thin films) or drop-casting (for monoliths or powders) methods to obtain fresh LLC films or thicker gels, respectively. The thickness of the films can be varied by spin rates or by controlling the volatile solvent (ethanol or water) amounts in the solutions. The spin-coating was done at a spin rate of 2000 rpm for 10 s. This ensures immediate solvent evaporation and gelation. Drop-casting was employed by spreading a few drops of the clear solution over a glass substrate. The drop-coat samples were kept for 2–3 min under laboratory conditions before inserting them into a preheated oven. This ensures the evaporation of the volatile solvent from the medium to form the gel mesophase. Then, the films were calcined at various temperatures (at 250, 300, 350, 400, 450, 500, and 700 °C) to produce mesoporous metal cobaltates (m-MCo$_2$O$_4$) films. The annealing time was 1 h at each temperature.

**Characterization.** POM images of the gel phases were recorded using a ZEISS Axio Scope A1 polarizing optical microscope. XRD patterns were collected using a Rigaku MiniFlex diffractometer, equipped with a Cu Kα (λ = 1.54056 Å) X-ray source, operating at 30 kV/15 mA and a Scintillator NaI(Tl) detector with a Be window and a Panalytical X’Pert pro multipurpose X-ray diffractometer equipped with a Cu Kα (λ = 1.5405 Å) X-ray source, operating at 45 kV/40 mA. N$_2$ adsorption–desorption isotherms were collected using a Micromeritics Tristar 3000 automated gas adsorption analyzer in the range of 0.01 to 0.99 P/P$_0$. Around 150 mg of sample was dehydrated under a vacuum of 35–40 mTorr at 200 °C for 2 h prior to the...
measurement. Saturated pressure measurements were repeated every 120 min during a 6−10 h measurement. The SEM images were recorded using a FEI Quanta 200 F scanning electron microscope on aluminum sample holders. The XPS spectra were collected using a Thermo Scientific K-α X-ray photoelectron spectrometer operating with a Al Kα micro-focused monochromatic source (1486.68 eV and 400 μm spot size) along with a flood gun for charge neutralization. The scraped powder samples from fluorine-doped tin oxide (FTO) electrodes were put on a copper tape for XPS analysis and the data were calibrated using the C 1s peak and/or O 1s peak. XPS spectra of the electrode surface were also recorded by directly inserting the FTO-coated films into the spectrometer and making a contact between the electrode surface and the spectrometer to avoid any surface charging. The electrochemical studies were carried out using m-MCo2O4-coated FTO as a working electrode (WE), Pt wire as a counter electrode, and Ag/AgCl (3.5 M KCl) electrode as a reference in a polypropylene cell with 1.0 M KOH solution. The measurements were performed using a Gamry instrument (potentiostat-PC14G750). The measured potentials were corrected and reported as the reversible hydrogen electrode (RHE). Prior to electrochemical measurements, N2 gas was purged into the electrolyte solution for 15 min to get rid of any dissolved O2. Cyclic voltammetry (CV), chronoamperometry (CA), and chronopotentiometry (CP) measurements were performed subsequently for each electrode. CV curves of the m-MCo2O4 electrodes (WEs) were recorded in the potential range of 0.2 to 2.2 V (vs RHE) with a scan rate of 50 mV/s. For each cyclic voltammogram, three cycles were recorded, and the second cycle was presented without IR compensation. In the CA measurements, a pre-determined potential was applied to the WEs to collect the current data. During the experiment, the electrolyte solution was stirred using a magnetic stirrer. At each potential, the potential was applied for 5 to 10 min, depending on how quickly a stable current level was reached; the last current data point is reported and used for further analysis. Tafel slopes were determined with the help of CA experiments. The starting potential for the OER is determined by the first CV and the earlier potential value is adjusted as a starting point for the CA experiment. The adjusted potential was then applied to the

Figure 1. XRD patterns of (a) fresh (black) and aged samples of NiCo-6; the inset shows the POM image of the aged sample, (b) NiCo-8 from spin-coated (0 min) to 30 min aging (with 5 min intervals), (c) NiCo-12 (0-fresh, 5, 10, 15−30 min-aged) samples (inset shows the POM image of the fresh sample), (d) POM image of 30 min-aged NiCo-12, and (e) ATR-FTIR spectral changes during solvent evaporation and molten salt (numbers are time in min).
WE by CA for 5 min and the current value at the end of the experiment was reported. This step was repeated with every 20 mV increments, and the current values were obtained for each applied potential. Then, the applied overpotential versus log(\(i\)) was plotted and the linear region was fitted to evaluate the Tafel slopes. The long-term CP and multistep CP experiments were carried at constant current densities of 1 and 10 mA/cm\(^2\) and 10 to 120 mA/cm\(^2\) with 10 mA/cm\(^2\) steps, respectively, to evaluate overpotential values required for the OER process. Potential data were collected for 1 to 48 h for long-term CPs and 30 min intervals for the multistep CPs while stirring the electrolyte solution using a magnetic stirrer. The last data point was reported as a voltage value of the CP experiment. The potential required for OER was then obtained by subtracting 0.424 V (0.424 V vs normal hydrogen electrode (NHE) from the Nernst equation \(E = E^\circ - 0.0592pF\), where \(E^\circ\) is 1.229 V and pH is 13.6) from the collected data to evaluate the overpotential values.

Electrochemically produced O\(_2\) gas was collected using a three-electrode cell, which is isolated using a parafilm, and the headspace of the flask (cell) was sealed with septa to determine the Faradic efficiency of OER. The reaction solution (1 M KOH) was purged thoroughly using N\(_2\) gas to remove any air in the electrolyte mixture for 30 min prior to each sampling for gas chromatography (GC) measurements. The CA experiment was conducted twice at 1 V (vs NHE) for 10 and 30 min for each electrode. The sample was taken from the headspace of the cell using a 100 μL syringe and injected into the GC system (Agilent 7820 A GC, equipped with a Molsieve column and a TCD detector) to detect the O\(_2\) and N\(_2\) gases each time. Ar was used as the carrier gas. Isolation and leakage tests were done by the N\(_2\) amount (for an ideal experiment, the N\(_2\) amount should remain constant throughout the experiment). The area under the peak of O\(_2\) is used for the calculation of O\(_2\) amount. Theoretical and experimental oxygen amounts were calculated using CA and GC data, respectively.

## RESULTS AND DISCUSSION

By adapting the MASA method, we have developed a new method to synthesize mesoporous MCo\(_2\)O\(_4\) thin films. Three different metal salts ([Mn(H\(_2\)O)\(_4\)](NO\(_3\))\(_2\), [Ni(H\(_2\)O)\(_6\)]\(^2-\), and [Zn(H\(_2\)O)\(_4\)](NO\(_3\))\(_2\)) have been chosen to demonstrate the versatility of the method and two different surfactant types (namely, C\(_{16}\)H\(_{33}\)N(CH\(_3\))\(_3\)Br, CTAB) were employed. C\(_{12}\)E\(_{10}\) and C\(_{16}\)H\(_{33}\)N(CH\(_3\))\(_3\)Br, CTAB) were employed. C\(_{12}\)E\(_{10}\) has been used in the synthesis of mesoporous MCo\(_2\)O\(_4\) (M = Mn(II) and Ni(II)) and P123 for NiCo-12 samples in their LLC phase. The mesophase is 2D hexagonal, see the inset in Figure 1a. POM images become dark above the mole ratio of 6. This corresponds to around 66 w/w % salt in the LLCP medium. This is an extremely high salt concentration and shows the flexibility and stability of LLCPs. However, at such high salt concentrations, the mesophase is not stable and quickly leaches out salt crystals (minutes). However, the LLCP becomes stable by decreasing the amount of salt, such that it is forever stable below a salt/surfactant mole ratio of 6. This corresponds to around 66 w/w % salt in the mesophase. Moreover, the mesophases are stable long enough for further processes (such as calcination) up to a mole ratio of 12. At salt/surfactant mole ratios higher than 12, the mesopores must be calcined immediately after coating to produce their mesoporous films.

The salt/surfactant mole ratio is important in further steps to hold the mesostructure during the calcination process. The LLCP of the samples was denoted MCo-# (M is Ni or Mn and # is the total salt to C\(_{12}\)E\(_{10}\) mole ratio). Figure 1 shows a series of small-angle XRD patterns and POM images of NiCo-6, NiCo-8, and NiCo-12 samples in their LLC phase. The mesophase is 2D hexagonal up to salt concentrations of 6, as evidenced from the fan texture in the POM image and XRD lines at small angles, see the inset in Figure 1a. POM images become dark above the mole ratio of 6, see the inset in Figure 1c, but these compositions still diffract at small angles and display characteristic XRD line(s) at small angles (see Figure 1c), together showing that the mesophase is cubic. Also note that the texture appears in the samples above salt ratios of 6 over time (upon aging the gel phase), indicating salt crystallization. Simply, the crystallization of excess molten salt reduces the salt/surfactant mole ratio below 6, at which point the mesophase is 2D hexagonal, see Figure 1b. Also note that at high salt concentrations, the salt crystallization is more obvious. Figure 1d shows a POM image of an aged sample of NiCo-12. It leaches out excess salt, indicating a metastable mesophase. The NiCo-12 sample shows diffraction at around 1.35° (d spacing is 65.4 Å) for 5 min, but the
diffraction line declines in time and a new line appears at around 1.74°, 2θ (d spacing is 50.7 Å), in 10 min; the small-angle line at 1.35°, 2θ, completely disappears in 15 min, see Figure 1c. The changes in the XRD pattern are due to salt crystallization which causes a shrinkage in the unit cell by 29% if we assume that both lines (at 1.35 and 1.74°, 2θ) originate from the same diffraction plane of the same phase. Also note that the changes in the XRD patterns are negligible up to a salt mole ratio of 6 but more drastic at higher salt ratios due to salt leaching and phase changes. Similar behaviors were also observed in the MnCo-# phases, see Figure S1.

In addition, we monitored the evaporation of excess water and the gelation process using ATR-FTIR spectroscopy (see Figure 1e). Clearly, there are several spectral changes in different regions of the spectra over time during the gelation process, such as the water-stretching and -bending regions (a broad feature at around 3200 cm⁻¹) as the water-stretching and -bending regions (a broad feature at regions of the spectra over time during the gelation process, such as the water-stretching and -bending regions (a broad feature at around 3200 cm⁻¹) as well as the modes at 1.35 and 1.74°, 2θ) originate from the same diffraction plane of the same phase. Also note that the changes in the XRD patterns are negligible up to a salt mole ratio of 6 but more drastic at higher salt ratios due to salt leaching and phase changes. Similar behaviors were also observed in the MnCo-# phases, see Figure S1.

The spectra at the bottom were recorded from the molten salt in the nitrate and water mixture to stabilize the mesophases at high salt concentrations. Therefore, 1 and 5 CTAB units per C₁₂E₁₀ and P123, respectively, were added to the medium to stabilize the mesophases at high salt concentrations, as established previously. However, the presence of CTAB in the medium also causes crystallization of the [CTA]₂[MBr₄] complex surfactant. Also notice that the crystals that leached out from the ZnCo-30 sample, after 1 day aging in the gel phase, are of the complex surfactant. However, the latter composition only leaches out salt crystals, see Figure S2. Simply, the complex surfactant crystallization could be hindered by increasing the salt concentration in the medium. Similarly, salt crystallization may be hindered to some extent by increasing the CTAB concentration in the medium. Moreover, salt crystallization is a slow process and may be avoided if one can calcine the fresh samples, as in spin-coating, or one can use CTANO₃ as a charged surfactant; however, its preparation requires tedious steps. Therefore, we have used CTAB as a charged surfactant and the calcination was carried out immediately after coating.

Mesoporous MCo₂O₄ (M = Mn(II), Ni(II), and Zn(II)) Thin Films and Monoliths. The Ni(II)−Co(II)−C₁₂E₁₀ system has been investigated in detail using seven solutions (with salt to surfactant mole ratios of 6, 8, 10, 12, 15, 20, and 25).

Drop-casting was also employed to obtain samples in large quantities as monoliths. Both spin-coating and drop-casting, followed by calcination yield samples that display similar N₂ adsorption–desorption isotherms and XRD patterns. Therefore, the spin-coating method has been used to produce thin films of LLCM films. Spin-coating was also employed to obtain samples in large quantities as monoliths. Both spin-coating and drop-casting, followed by calcination yield samples that display similar N₂ adsorption–desorption isotherms and XRD patterns. Therefore, the spin-coating method has been used to produce thin-film electrodes (see later), but the drop-casting method was used where a large amount of sample was required, such as in the measurements of N₂ adsorption–desorption isotherms and XRD patterns. The calcined mesoporous samples are denoted m-NiCo₂O₄−n-XXX (where n is the salt–surfactant mole ratio and XXX is the calcination temperature).

Figure 2a shows a set of XRD patterns of monoliths, calcined at 250 °C. Clearly, even at 250 °C, the resulting samples are crystalline, and the diffraction lines can be indexed to spinel NiCo₂O₄. The diffraction lines become sharper with increasing calcination temperature, see Figure 2b. The crystallite size, calculated using Scherrer’s equation, increases from 4.5 to 12.4 nm by increasing the calcination/annealing temperature from 250 to 500 °C, respectively, see other particle sizes at other
temperatures in Table 1. There is no secondary phase in the samples of m-NiCo2O4-n-250 (n is 10 and above), but the

<table>
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samples prepared using salt/surfactant mole ratios of 6 and 8 also display weak secondary lines due to the metal hydroxide species. However, these two samples are also crystalline spinel NiCo2O4 at 300 °C and above. On further annealing or direct calcination at around 500 °C, two new very weak lines appear at 43.5 and 63.2°, 2θ, due to (200) and (220), respectively, of rock salt NiO. With further annealing, these lines and some new lines of NiO merge and intensify. This is commonly observed in the spinel NiCo2O4 phase in the literature. The origin of the NiO phase may be due to either phase separation of m-NiCo2O4 into NiO and Co3O4 phases or crystallization of amorphous NiO domains in the pore walls. To test this, m-NiCo2O4 was further annealed step-by-step from 550 to 700 °C, see Figure 2c. Note that mesoporous NiO synthesized by MASA crystallizes at around 300 °C and becomes highly crystalline over 400 °C. However, the crystallization of NiO domains may be hindered due to strong NiO–NiCo2O4 interactions at the interface on top of the films or within the pore walls. Also notice that the intensity of NiO lines increases more than that of the NiCo2O4 lines with annealing at higher temperatures, indicating a phase separation, but this still may not be sufficient evidence to overrule the growth of NiO coming out from the surface and between the NiCo2O4 domains of the pore walls. Also note that there is no change in the NiCo2O4 lines other than sharpening with further crystallization.

The same samples were also used to collect N2 adsorption–desorption isotherms and pore-size distribution plots. Clearly, all samples are mesoporous at all compositions. The isotherms are typical, type IV, and characteristic for the mesoporous materials. The pore-size distributions become less uniform with the increase of salt amount in the mesophase (see Figure S3). Table 2 shows the Brunauer–Emmett–Teller (BET) surface area, Barrett–Joyner–Halenda (BJH) pore volume, and BJH pore size of m-NiCo2O4-n-250. Among these samples, the highest surface area was recorded to be 223 m²/g from the m-NiCo2O4-10-250 sample. All samples display similar pore volumes, but the pore size gradually increases from 3.5 to 6.0 nm with the increase of n from 6 to 25, respectively; comparison data are provided in Table 2. Since the highest surface area was obtained from a mole ratio of 10, m-NiCo2O4-10 was further investigated at higher temperatures. Figure 3a,b shows the changes in the N2 adsorption–desorption isotherms and pore-size distributions of m-NiCo2O4-10-XXX (where XXX was varied between 300 and 500 °C). The surface area of the sample decreases with increasing calcination temperature (from 172 m²/g at 300 °C to 31 m²/g at 500 °C). Similarly, the pores expand from 6.9 to 25.6 nm. However, the pore volume remains almost unaltered, indicating that the pores are expanding at the expense of smaller pores. Details of the N2 adsorption–desorption data are tabulated in Table 2.

SEM and TEM images of the samples were also obtained to show the film morphology and pore system. Figure 4a–c show SEM images of samples obtained at mole ratios of 6, 15, and 25. Clearly, the samples with mole ratios of 6 and 15 have uniform film morphologies, but the m-NiCo2O4-25 sample is more fragile and less rigid. The mesopores of the samples, calcined at higher temperatures, are resolved and clearly visible in the SEM images of the samples; for samples calcined at 450 and 500 °C, see Figure 4d,e. Figure 5 shows a set of high-angle annular dark-field STEM and TEM images of m-MCo2O4 samples. The sponge-like pores are clearly visible but disordered throughout the films, see Figure 5a,b. The pore walls are constructed of crystalline nanoparticles of MCo2O4, see Figure 5c. Both SEM and TEM images accord well with the N2 adsorption–desorption data and XRD patterns.

MnCo2O4 samples were also prepared using the same method and compositions. Freshly prepared and aged samples of the Mn(II)–Co(II)–C12E10 system were extensively investigated using seven different compositions (total salt/C12E10 mole ratios of 6, 8, 10, 12, 15, 20, and 25) from solution to gelation and then to calcination. MnCo# samples behave like the NiCo# samples. Both Mn(II) and Co(II) salts synergistically affect each other’s miscibility and phase stability. Even at a salt/surfactant mole ratio of 12, the mesophase is stable for long periods, see Figure S1. All compositions were calcined and investigated (details of all compositions are given in the

Figure 3. (77 K) N2 adsorption–desorption isotherms (a) and pore-size distribution plots (b) of m-NiCo2O4-10-XXX samples [XXX is (I) 250, (II) 300, (III) 350, (IV) 400, (V) 450, and (VI) 500 °C].
Supporting Information section, Table S1), but most of the efforts have been devoted to composition with a (Mn(II)+2Co-(II))/C12E10 mole ratio of 10. Samples prepared at those compositions were further characterized (by recording their temperature-dependent XRD patterns and N2 adsorption−desorption isotherms) and investigated electrochemically (see later). Clearly, the spinel m-MnCo2O4 forms at as low as 250 °C, see Figure S4a. However, the growth of the pore walls is postponed until 550 °C. Table 1 lists the size of the MnCo2O4 nano-crystallites, calculated using Scherrer’s equation and the (311) line in the XRD patterns. The XRD lines are quite broad up to 500 °C (particle size increases only 30%, from 4.4 to 5.7 nm by annealing from 250 to 500 °C), but above 550 °C, the nanocrystalline MnCo2O4 pore walls grow (it is 8.2 nm at 550 °C, another 44% growth and then it grows to 19, 26, and 49 nm at 600, 650, and 700 °C, respectively); however, no phase

Table 2. N2 (77 K) Adsorption−Desorption Data of m-NiCo2O4-n-XXX, m-MnCo2O4-n-XXX, and m-ZnCo2O4-XXX (20:40 Zn/Co Mole Ratio). SA Is the BET Surface Area, PV Is the BJH Pore Volume, and PS Is the BJH Pore Size

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<th>sample</th>
<th>$S_{BET}$ (m²/g)</th>
<th>$V_P$ (cm³/g)</th>
<th>$D_P$ (nm)</th>
<th>Sample</th>
<th>$S_{BET}$ (m²/g)</th>
<th>$V_P$ (cm³/g)</th>
<th>$D_P$ (nm)</th>
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</table>

“BET surface area determined from the linear part of BET equation ($P/P_o = 0.05–0.25$). Total pore volume determined as $P/P_o = 0.99$. Pore diameter from the desorption branch.

Figure 4. SEM images of m-NiCo2O4-#-300, where # is (a) 6 (inset is a 4 times magnified small part of the image), (b) 15, and (c) 25. SEM images of the sample calcined at (d) 450 and (e) 500 °C.

Figure 5. (a) HAADF image of m-NiCo2O4-10-350 (inset is 4 times magnified image) and (b,c) TEM images of m-MnCo2O4-10-350 at different magnifications.
separation was detected, see Figure S4a. The N2 adsorption−desorption isotherms were in well accord with the XRD results, see Figure S4b,c. The pore size shows almost no change up to 550 °C with a relatively smaller pore size, see Figure S4c and Table 2. Clearly, the MnCo2O4 domains resist growth upon annealing, as opposed to NiCo2O4 and ZnCo2O4 (see later).

The SEM image of the samples shows a uniform film morphology at low salt/surfactant ratios (6 to 12) but becomes rougher at higher ratios (15 to 25), see Figure S5. The cracks are due to film thickness. Note that the thinner films (spin-coated once) are uniform and crack-free. TEM images show a sponge-like porous network made of 5−6 nm MnCo2O4 particles (see Figure 5b,c).

The ZnCo2O4 samples were prepared using P123 as the main surfactant and CTAB as the co-surfactant with a 1:5 P123/CTAB mole ratio. The P123 system has been investigated at three different compositions, but the intermediate composition (20Zn(II):40Co(II)) yielded a mesoporous thin film with the highest surface area. Therefore, this composition has been investigated more in detail. The 10Zn(II)/20Co(II)/1P123 samples were also stable both in the mesophase and mesoporous forms. However, high salt samples (30Zn(II)/60Co(II)/1P123) were problematic in the gel phase and leached out salt species prior to calcination. Therefore, this composition was only investigated in the gel phase. The mesoporous films were labeled m-ZnCo2O4-30-XXX and m-ZnCo2O4-60-XXX (m stands for mesoporous and 30 and 60 are (Zn(II)+2Co(II))/P123 mol ratios and XXX is the calcination/annealing temperature). Figure 6 shows a set of XRD patterns of m-ZnCo2O4-60-XXX calcined at various temperatures from 250 to 550 °C. Clearly, all diffraction lines can be indexed to spinel ZnCo2O4. No other phase or composition was detected in the patterns at all temperatures, see Figure 6a. The only change with increasing temperature was the sharpening of the diffraction lines. Table 1 lists the size of the nanocrystallites making the pore walls, as calculated using Scherrer’s equation and the (311) line in the XRD patterns. Figures S6a and S7 show an SEM image of m-ZnCo2O4-60-400 and a set of TEM images of m-ZnCo2O4-60-350 and display a smooth film morphology and uniform pores. The films have disordered sponge-like pores with crystalline pore walls, see Figure S6.

HR-TEM images of m-NiCo2O4-350, m-MnCo2O4-350, and m-ZnCo2O4-350 and their analysis are shown in Figure S8. Lattice fringes are clearly visible and spacings between the lattice fringes are consistent with the d-spacings of the XRD lines that originated from the (111) planes. Also notice that the size of the crystalline domains on the pore walls (~5, 9, and 8 nm in the m-NiCo2O4, m-MnCo2O4, and m-ZnCo2O4 samples, respectively, compare with the data in Table 1) are similar to that predicted from Scherrer’s equation using (111) XRD line broadenings. Figure 6b,c shows the N2 adsorption−desorption isotherms and pore-size distribution plots, respectively. Isotherms are type IV, characteristic for mesoporous materials. The pore-size distribution becomes less uniform at higher temperatures but remains more ordered, relatively, compared to m-NiCo2O4. The pore-size expansion was limited (4−11 nm) in the m-ZnCo2O4 samples. We also tested annealing (first calcined at 250 °C and then annealed at higher...
temperatures) versus direct calcination at a given temperature to establish a simple method. Both sets gave similar isotherms and pore-size distribution plots, see Figures 6c and S6b. However, the direct calcination at 300, 350, and 400 °C yields a more uniform pore-size distribution that may be necessary for certain applications, compare Figures 6c and S6b.

We also checked the 60 (Ni(II)+2Co(II)/P123 sample to determine if the surfactant plays a role in the order of mesopores. Figure S9 shows a set of PXRD patterns, N2 adsorption−desorption isotherms, and pore-size distribution plots of m-NiCo2O4-60-XXX samples. The XRD patterns, N2 adsorption−desorption isotherms, and pore-size distribution plots are all remarkably similar to those of samples prepared using C12E10 mesophases. Similarly, the NiO phase appears at high-annealing temperatures and pores become disordered and large; the surface area is 175 m2/g at 250 °C, but it gradually decreases to 25 m2/g at 500 °C, and similarly the pores expand from 3.9 to 15.4 nm at those temperatures. We can therefore conclude that the surfactant type is not as important for these materials.

**Electrochemical Properties of m-MCo2O4 (M = Mn(II), Ni(II), and Zn(II)) Thin Films.** The electrodes of m-NiCo2O4, m-MnCo2O4, and m-ZnCo2O4 were prepared by spin-coating their freshly prepared solutions at their optimum compositions over a 1 × 1 cm2 FTO substrate. The calcined films were then used as the WE in all electrochemical characterization and the OER. Figure 7a shows a set of cyclic voltammograms (CV curves) of the m-NiCo2O4 electrodes, calcined at indicated temperatures. Figure 8b shows the Tafel plots of the same electrodes. The Tafel slope (AT) gradually decreases from 63 to 49 mV/dec by increasing the annealing temperature, see Figure 7b and Table 3. Clearly, with increasing calcination/annealing temperature, the peak currents of the Faradaic process decrease and accord well with the reduced surface area of the electrodes. A typical electrode has a mass of 0.1 mg/electrode. Such a high current density observed in the Faradaic process is an indication of the accessibility of the pore surface (internal surface) of m-NiCo2O4 electrodes. The peak at around −0.2 V has been previously assigned to the NiO phase (Ni2+/Ni3+). Later peaks at higher potentials are due to other Ni2+/Ni3+, Ni3+/Ni4+, and Co3+/Co4+ oxidation processes over the electrode surfaces, see the inset in Figure 7a. Although surface-active species, they are likely the active species for the OER process, which gradually decreases with increasing annealing temperature (with decreasing surface area), the slope of the OER process (over 1.4 V)

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<th>sample</th>
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<th>η1 (mV)</th>
<th>η10 (mV)</th>
<th>η100 (mV)</th>
<th>η10 (mV)</th>
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Overpotentials: 2h and multistep CP experiments and calculated after IR compensation using multistep CP data. R100 is the predicted electrode resistance at 100 mA/cm2 current density.

Figure 8. CV curves of m-MnCo2O4-10-XXX (XXX values are given in the panels) (a) before and (b) after multistep CP experiments (insets show Faradaic regions of the same CV curves).
increases at 350 °C with almost no change up to 500 °C. If we normalize our CV curves to the surface area of the actual electrodes (by dividing the current density to the surface area of a 0.1 mg electrode to compensate the reduced surface area at higher temperatures), the current density gradually increases with increasing temperature (crystallization), see Figure S9; the current densities are 1.88, 3.94, 4.99, 6.64, and 8.47 A/m² at 300, 350, 400, 450, and 500 °C at 2.0 V versus RHE, respectively. The current density increases linearly with increasing annealing temperature, like the particle size and crystallinity, see the inset in Figure S10. The normalized CV curves also demonstrate that not only the surface area but also the crystallinity of the pore walls is important in the OER. Therefore, the ideal targeted electrodes should have a high surface area with high crystallinity. The overpotential values evaluated from the long-term CP experiments (see Figure S11a,b) are lower than those of both NiO, 38 Co₃O₄ 48 and other spinel-transition-metal oxides (see Table S2). 17,48–56

The m-NiCo₂O₄ electrodes have also been used for CP experiments at 1 and 10 mA/cm² current densities for 2 h each and for multistep CP experiments for a duration of 30 min at each current density starting from 10 to 100 mA/cm² with 10 mA increments for 5.5 h, see Figure S11a,b. Potential (calculated using \( V_1 - A_1 \log(j) \), where \( V_1 \) is the potential at each current density \( j \)), \( A_1 \) is the Tafel slope, and \( j \) is the current density, obtained from multistep CP experiments) versus current density is linear, where the slope is the resistance of the electrode (R), see Figure S11c. R is equal to \( (V_{100} - V_{10}A_1)/\Delta I \) (where 10 to 100 mA is a decade, \( \Delta I = 90 \) mA, and \( V_{10} \) and \( V_{100} \) are potentials at 100 and 10 mA/cm² current densities, respectively), see Table 3 and Figure S9c. Also, note that the electrode resistance predominantly originates from the FTO substrate. The resistance of m-NiCo₂O₄-10-300 is 17.3 and of m-NiCo₂O₄-10-350 is 13.6 Ohms, see others in Table S3. Clearly, the IR drop is the lowest in the m-NiCo₂O₄-10-350 electrode that displays the best OER performance.

The CV curves before and after long-term CP experiments were also recorded to monitor the stability of the electrodes and any change in the surface chemical species. Figure S12 compares CV curves before and after multistep CP experiments. Clearly, the peak current at around 1.1 V increases after the CP experiments. This peak has also been observed in mesoporous NiO after CP experiments. The NiO surface is covered with NiOOH/Ni(OH)₂ surface species. The peak at 1.1 V has been assigned to the oxidation of Ni(OH)₂ to NiOOH species (Ni²⁺/Ni³⁺) 38 and is consistent with the XRD pattern, which also displays NiO lines in the m-NiCo₂O₄ electrodes. The peak(s) at higher potentials (around 1.3 V vs RHE) could be assigned to the oxidation of Ni³⁺ and Co³⁺ species to their 4⁺ species, which are the active species in the OER process. 38,56 It has been demonstrated previously that the rock salt NiO is converted to a NiO−NiOOH core−shell structure. The NiOOH layer is converted, upon reverse cycling (reduction process), to layered Ni(OH)₂, which is more active than NiO. Under harsh oxidation conditions (such as at 100 mA/cm² current density), more active surface species are produced over the m-NiCo₂O₄ electrode surface; as a result, the electrodes work at relatively lower overpotentials. Notice that the overpotentials at 100 mA/cm² current density, after a correction by subtracting the IR drop (\( n_{100} \), calculated in Table 3), are even lower than the ones at 1 mA/cm² current density in m-NiCo₂O₄-10-XXX (XXX is 300, 350, 400, and 450 °C) but are reasonable in the samples annealed at higher temperatures (500 and 700 °C), see Table 3.

Since the overpotential could not be lower at higher current densities, the actual electrode resistance must decrease with use in the OER at higher current densities; the electrode becomes a better conductor. If we assume that the overpotential increases by \( 2A_1 \) by increasing the current density from 1 to 100 mA/cm², then the actual overpotential must be at least 330 mV in the m-NiCo₂O₄-10-300 electrode. However, the measured overpotential is 1932 mV for this electrode, due to overpotential (330 mV) plus IR drop (1620 V). Therefore, the electrode resistance is 16.2 Ω (calculated using Ohm’s law, \( R = (V_{100} - V) / 100 \), where \( V_{100} \) is the measured potential (1932 mV) and \( V \) (330 mV) is the calculated overpotential at 100 mA/cm² current density) or lower after the multistep CP experiment. Table 3 lists the electrode resistances together with the resistance after the CP experiment to demonstrate that all electrodes display lower resistance and better performance with use for OER at high current densities.

Similar electrochemical data have also been collected using m-MnCo₂O₄-10 electrodes. Figure 8a shows a set of CV curves of m-MnCo₂O₄-10 electrodes, calcined at five different temperatures. The m-MnCo₂O₄-10-350 electrode performs the best in the OER, but the other electrodes, calcined at higher temperatures, also display a similar performance. As previously shown by the XRD patterns and \( N_2 \) adsorption–desorption isotherms, the m-MnCo₂O₄ samples resist heat treatments. The CV curves and OER performance of these electrodes are also similar. Overpotential values are slightly higher than those of m-NiCo₂O₄ electrodes, but the \( A_1 \) values are clearly higher, see Table 3 and Figure S13; they increase with increasing annealing temperature. For instance, the \( A_1 \) value of the m-MnCo₂O₄-10-300 electrode is like that of m-NiCo₂O₄ electrodes, but it gradually increases up to 85 mV/dec in m-MnCo₂O₄-10-500, indicating a change in the OER mechanism and likely the surface chemistry. We also performed the CP experiments at 1 and 10 mA/cm² current densities for a duration of 2 h each and multistep CPs starting from 10 to 100 mA/cm² with a 10 mA increment for 30 min at each current density for another 5.5 h, see Figure S14a,b. The electrode resistance has been evaluated using the multistep CP data and by considering the change in the Tafel slopes, see Figure S14c and Table 3. Clearly, the change in R is negligible in the m-MnCo₂O₄-10-XXX electrodes with use under harsh conditions (high current densities), indirectly indicating the electrode stability. Moreover, the CV curves after CP experiments were also recorded to check the stability of the electrodes and investigate the chemical changes on the electrode surfaces, see Figure 8b. The m-MnCo₂O₄-10-300 electrode shows a significant/visible change in the CV curve after the multistep CP experiment. Also note that this electrode has the highest resistance (23.8 Ohms) and the lowest Tafel slope. The peak observed at around 0.72 V, likely due to the oxidation of Mn²⁺ to Mn³⁺, almost disappears, and a new peak at around 1.1 V forms due to the oxidation of Mn³⁺ to Mn⁴⁺ or of Co³⁺ to Co⁴⁺; however, the change in CV curves is less in the m-MnCo₂O₄-10-350 electrode and almost none in all other electrodes, calcined above 400 °C. Likely, at low temperatures, there is some Mn²⁺ species on the electrode surface and eliminated during the CP experiment over the m-MnCo₂O₄-10-300 electrode. The Mn²⁺ species (maybe in the form of MnO) at low temperatures is dissolved during long-term CP experiments; however, Mn²⁺ in the spinel structure resists solvation. This behavior is also visible in \( A_1 \) values; the \( A_1 \) is like CoO₂ at low temperatures (62 mV/dec, maybe indicating more Co³⁺ species by dissolving Mn²⁺ species over the m-MnCo₂O₄-10-300 electrode surface), but it
increases to the 78–85 mV/dec range after annealing the electrodes over 400 °C. As suggested in our previous work on LiMn$_2$Co$_x$O$_4$ electrodes, such as Mn$^{2+}$ and Co$^{3+}$, the surface species collectively work in the OER process. It has been well established that pure LiMn$_2$O$_4$ (manganese is Mn$^{3+}$ and Mn$^{4+}$) is not stable in electrochemical processes due to disproportionation reactions ($2\text{Mn}^{3+}$ species undergo disproportionation to Mn$^{2+}$ and Mn$^{4+}$ species and dissolution of Mn$^{2+}$ sides); however, the presence of cobalt stabilizes the manganese–cobalt-oxide surface species and synergistically (electronic) work together in the OER process. Also notice that the electrode stability is also reflected in the overpotential values after IR compensation. The overpotential increases as a function of logarithm of $A_T$ with increasing current density. The electrode resistance, after the multistep CP experiment, changes little. Although the overpotential values are slightly higher with a slower OER rate in m-MnCo$_2$O$_4$ electrodes, they are more stable and resistive to heat treatments. Thermal stability also brings electrochemical stability to these electrodes.

The CV curves of both set of m-ZnCo$_2$O$_4$ samples (calcined at 250 °C, then annealed at different temperatures, and directly calcined at the tested temperature, and labeled m-ZnCo$_2$O$_4$-an and m-ZnCo$_2$O$_4$-d, respectively) were also obtained and are displayed in Figure 9. The only peak at around 1.4 V is due to the oxidation of Co$^{3+}$ to Co$^{4+}$, see the inset in Figure 9a. No trend was observed in the annealed electrodes in terms of stability and OER performance. However, the directly calcined m-ZnCo$_2$O$_4$-d electrodes show excellent stability in long-term use at high current densities in the oxygen evolution process. Note that all the electrodes were fabricated using the salt/P123 mole ratio of 60. Since there is a trend in OER performance and the electrodes are stable to long-term CP experiments, the m-ZnCo$_2$O$_4$-d samples were also investigated in detail. Figure 9b shows the CV curves of the freshly prepared electrodes. Like the m-NiCo$_2$O$_4$-350 and m-MnCo$_2$O$_4$-10-350 electrodes, the directly calcined m-ZnCo$_2$O$_4$-d-350 displays the best electrode performance among the five electrodes prepared at 300, 350, 400, 450, and 500 °C. Moreover, the m-ZnCo$_2$O$_4$-d-500 electrode performs as good as the m-ZnCo$_2$O$_4$-d-350 electrode in long-term CP tests. Comparing all three electrodes, m-MCo$_2$O$_4$-n-350 (where M is Ni and Mn, n is 10; for M is Zn, n is 60), it appears that 350 °C is an ideal calcination temperature to fully evacuate the pores and make the internal surface accessible for the electrochemical process. Figure 9c shows the CV curves after multistep CP experiments and shows the stability of the m-ZnCo$_2$O$_4$-d-XXX electrodes. All electrodes displayed almost identical CV curves after long-term use under harsh conditions. Interestingly, some electrodes performed even better after used in the CP experiment. For example, both m-ZnCo$_2$O$_4$-d and m-ZnCo$_2$O$_4$-an electrodes, calcined directly at and annealed to 500 °C, respectively, improved the most. This shows that the crystallinity of the electrodes is particularly important to further improve the OER performance of the electrodes. The $A_T$ values of m-ZnCo$_2$O$_4$ electrodes fluctuate at around 52–60 mV/dec, like in the m-NiCo$_2$O$_4$ electrodes (see Table 3 and Figure S15a).

Figures S15b and 9d show the CPs at 1 and multistep CPs from 10 to 100 mA/cm$^2$ current densities, respectively. The CP data can be used to determine the electrode resistances, which are the slope of the potentials (determined at each current density, 10 to 100 mA/cm$^2$) versus current density plots, see Figure 9e. After subtracting the IR drop values, the electrode overpotentials drop to 226, 280, and 345 mV at 1, 10, and 100 mA/cm$^2$ current densities, respectively, in the m-ZnCo$_2$O$_4$-d-350 electrode with increments of 54 and 55 mV close to $A_T$ (54 mV/dec), see Table 3. However, if we assume that the reaction mechanism and the reaction rate (Tafel slope) do not change during the multistep CP experiment, then the calculated $\Delta R$ varies within 1.0 Ω, indicating high stability of the electrodes under harsh conditions. The major losses, at high current densities, are due...
to IR drops that can be mostly overcome using better conductive substrates, such as carbon or metals. Figure 9f shows two CV curves before and after IR correction, showing a sharp increase in the current density over the potentials at which the OER process takes place and is consistent with the Tafel slope.

We also performed a CA experiment to determine the Faradaic efficiency of the best-performing electrodes, namely, m-NiCo₂O₄-350, m-MnCo₂O₄-350, and m-ZnCo₂O₄-350. The produced O₂ amount was determined using GC, see Table S3. Both m-NiCo₂O₄-350 and m-ZnCo₂O₄ electrodes perform better with use; their Faradaic efficiency reaches 92 and 73%, respectively, in 30 min. However, the m-MnCo₂O₄ displays over 93% Faradaic efficiency in 10 min.

OER Mechanism over the m-MCo₂O₄ (M = Ni, Mn, and Zn) Electrodes. The OER mechanism, suggested in our previous work,[39] is modified and updated in Figure 10a. Originally, Wang et al.[16,59] suggested a six-step OER mechanism based on a nucleophilic acid–base reaction that considers a nucleophilic attack of hydroxide in the medium to metal oxo (M = O, formed either by oxidation or reaction of two metal hydroxides, see Figure 10a) species to form a O–O bond. The mechanism is based on the electroneutrality principle, electro-negativity of the likely surface species, and some experimental evidence. The electronegativity difference between two metals (indicated as M and M’) is the driving force for the first and second steps (formation of M═O and nucleophilic attack of the hydroxide ion to the metal oxo side for the O–O bond formation, M–OOH). Also, the high affinity for water (as evidenced from DFT calculations[19]) to the M’ side synergistically amplifies the OER. Also, note that the formation of M═O, M–OOH, and superoxide (O₂⁻) has also been identified by in situ ATR-FTIR studies during the electrochemical process and/or later analysis of the used metal oxide electrodes.[60–63]

A qualitative molecular orbital (MO) energy level diagram, which would be useful to understand the formation and role of the metal–oxygen double bond (metal–oxo bond, M═O) was constructed using metal d-orbitals and oxygen 2pₓ and 2pᵧ orbitals, see Figure 10b. The MO diagram has been constructed by perturbing the local symmetry from octahedral to the C₆v point group by the formation of M═O along the z-axis, see the structure in Figure 10b. A partially or fully occupied doubly degenerate e(dₓz and dᵧz) orbitals of M interact with the occupied e(2pₓ and 2pᵧ) orbitals of oxo-oxygen, where the M═O π-bond strength is enhanced. Moreover, the electron donation from oxygen to the metal side also enhances the electrophilic character of the oxo-oxygen. Also, note that the strength of the π–π interaction in the metal–oxo bond strongly depends on the electronenegativity difference between the metal ion (which increases by oxidation to higher oxidation states) and the oxygen atom. Therefore, the formation of the M(IV) or M(V) side is important in the electrochemical process to increase the electrophilicity of M═O sides. Simply, a strong π-interaction pushes the π* e(dₓz, dᵧz) orbitals to higher energy and makes the complex high spin and half-filled in electron-rich systems such as Ni and Co, see Figure 10b. The calculated π-bond order using electrons of bonding (π) and antibonding (π*) orbitals for the oxo bond is 1.0 for d⁶Mn(IV), 1.5 for d⁷Mn(V), 1.0 for d⁶Co(IV), and 1.0 for d⁷Ni(IV) in their oxo species. This simple prediction accords well with our findings that all spinels, investigated in this work, perform well and in a similar manner. The suggested OER mechanism is similar to our previous proposal for the mesoporous LiMn₂₋₂CoO₄ thin-film electrodes.[59] Also notice that m-MCo₂O₄ and LiMn₂₋₂CoO₄ have spinel structures and likely have similar surface species. Briefly, water dissociation is an important process, where a hydroxide ion is used either for a nucleophilic attack to M═O or as a base to undergo an exchange reaction with coordinated water in necessary steps (inspect Figure 10a), as a result to produce hydronium ions (H₃O⁺) in steps 2, 3, 6, and 8; hydronium ions are necessary for the counter electrode reaction. M and M’ simultaneously undergo oxidation reactions to produce the necessary four electrons in steps 2, 4, 6, and 7 and a self-reduction to produce an oxo bond in step 1, a superoxide in step 5, and an oxygen molecule in step 8 in an overall water-splitting process.

To bring some insights into the suggested proposal, we also obtained high-resolution XPS spectra of O 1s, Mn 2p, Co 2p, Ni 2p, and Zn 2p regions before and after multistep CP experiments by directly using the coated FTO electrodes (top surface) and ground electrodes (internal pore surface) to determine the differences in the electrode surface and internal surface. Figure S16 shows a set of metal 2p (²P₁/₂, ²P₃/₂ region) high-resolution XPS
spectra of the FTO top surface and the internal surface of m-MnCo2O4-350 (M is Ni, Mn, and Zn) electrodes before and after CP experiments. Figures S16–S21 show the other set of XPS spectra of all electrodes. The O 1s peaks provide insightful information regarding surface species, see Figure S17. The peak at 529.9 eV has been assigned to lattice oxygens.64,65 The shoulder that becomes the main peak in some cases on the high-energy side can be convoluted into three peaks at 530.5, 531.2, and 532.3 eV due to hydroxyl, peroxo, and coordinated water species, respectively, see Figure S17. The O 1s spectra of the electrode over FTO (reflects the electrode top surface) and ground samples (provide more internal surface) display clear differences, see Figures S17 and S18. Hydroxide, peroxo, and coordinated water peaks are generally enhanced in the internal surface of the electrodes. However, one must be careful using O 1s regions, because carbonate and graphene oxide-type species that may be likely products of calcination also appear in this region. Therefore, we instead focused on the transition-metal 2p regions, see Figure S16. Also note that the Mn 2p intensity increases by annealing the samples at higher temperatures, possibly indicating an enrichment of Mn species on the surface of m-MnCo2O4 electrodes, see Figure S19. This correlates with the Tafel slope, which also increases upon annealing. Manganese-rich surfaces have higher Tafel slopes.39 The coordinated water and peroxide species increased the most in m-NiCo2O4 electrodes after CP experiments, compare the spectra in Figure S18. The peak at around 531.5 eV becomes the major peak in m-NiCo2O4-10-350, which is the best-performing m-NiCo2O4 electrode. The origin of enhancement of the peak at 531.5 eV may be due to the formation of NiOOH and Ni(OH)2 species. Also, remember that the m-NiCo2O4 electrode has an NiO side product that undergoes transformation to NiO–NiOOH and NiO–Ni(OH)2 core–shell structures during the CP experiment.38 Note that the hydroxide species on both NiOOH and Ni(OH)2 are not terminal surface hydroxides (coordinated to one metal ion), instead they are coordinated to three Ni2+ ions in layered NiOOH and Ni(OH)2. Therefore, the O 1s peak appears at around 531.5 eV. The Ni 2p spectra also corroborate this, see Figures S16b and S20b,d. The peak at around 855.1 eV is due to Ni2+ (NiO) that decreases over time during the CP experiment and the peak at around 856.3 eV becomes the major peak after the CP experiment, indicating the enrichment of Ni2+/Ni3+ (Ni(OH)2 and NiOOH) species at the surface. Clearly, from both O 1s and Ni 2p regions, the surface of m-NiCo2O4 changes after the CP experiments, compare spectra in Figure S16b and S20. Moreover, the changes in m-MnCo2O4 in all regions, namely, O 1s, Co 2p, and Mn 2p are quite small. The Mn 2p spectra display peaks due to Mn2+, Mn3+, and Mn4+ species, see Figure S16d. Overall, changes in the metal 2p spectra (other than Ni 2p) are negligibly small, indicating the stability of the m-MnCo2O4 electrode surfaces, as we predicted from the electrochemical analysis in the previous section. The Co 2p region of all three electrodes (top surface and internal surface before and after use in CP experiments) was also recorded, as it is the other common element in three structures. Note that it is difficult to evaluate the oxidation state of cobalt (similarly for Mn and Ni) due to the complexity of the 2p line shape, which consists of peaks from multiplet splittings66 (due to coupling between the unpaired 2p electron and unpaired valance electrons), oxidation states, and also overlapping of the satellite peaks. However, the satellite peaks of cobalt species are well resolved from the main peak and appears at 786 eV for Co(II) and at 790 eV for the Co(III) and Co(IV) species (see the Co 2p spectra in Figures S16a,e and S19–S21). Also note that it is an accepted practice to use the satellite peaks for determining the oxidation state of cobalt species.66 Based on this information, we can conclude that both the m-NiCo2O4 and m-MnCo2O4 surfaces contain both Co(II) and Co(III)/Co(IV) sides; however, in m-ZnCo2O4, almost no Co(II) sides are detected. This is also clear from the Zn 2p region (Figure S21b,d) that displays simple Zn(II)-related peaks at 1021 and 1044 eV due to 2P1/2 and 2P3/2 spin–orbit states, respectively.67 Since Co is in the 3+ oxidation state in m-ZnCo2O4 only the satellite peak that originates from the Co(III) side and the main 2P3/2 peak become more symmetric, because Co(III) species with a d5 low-spin electron configuration (all valence electrons are paired) is not subjected to multiplet splitting. Detailed XPS analyses show that all metal species used in our proposal were detected and consistent with our mechanism.

We also evaluated the anodic charge-transfer coefficient (α) of electrodes using Tafel slopes (AT values, where AT = 2.303RT/(nαF) = 59.2/(nαT)) vs. the temperature, n is the number of electron transferred, and F is Faraday’s constant) to support our proposal, see Table 3. It is a useful number for determining the rate-determining step in the OER process68,69 Since more than one electron transfer is unlikely in a single step, α is considered to be one.67 Therefore, α is equal to 59.2/AT. The charge-transfer coefficient of both m-NiCo2O4 and m-ZnCo2O4 electrodes is remarkably similar and around one. It means that the rate-determining step involves a chemical step after the first electron-transfer step in the OER process, as suggested in step 2 (see Figure 10a). However, the α value gradually decreases from 0.95 (in m-MnCo2O4-10-300) up to 0.70 (in m-MnCo2O4-10-450). Also note that in our previous work on mesoporous LiMnO4 where both metals are manganese and are in 3+ and 4+ oxidation states, the Tafel slope is around 120 mV/dec with an α value of 0.5. As suggested by Doyl et al.,69 the first electron-transfer step in a sequential reaction is the rate-determining step in the m-MnCo2O4 electrodes. However, we have suggested the first electron-releasing step as the oxidation of M′(III) to M′(IV) rather than the oxidation of Mn(IV) to Mn(V).39 This was a reasonable suggestion as one would expect that the change of M′2+ to M′3+ would occur at a lower potential. However, if we consider the M′(II) species as M′(O)3(OH)2 and the Mn(IV) species as a tetrahedral (O= Mn(O)3) or octahedral (O= Mn(O)(OH)2), Sanderson’s electronegativity (χ) of likely surface species can be calculated from the geometric mean of electronegativity of the atomic constituents (such as χM′(O)3(OH)2 ≈ (χM′χO)1/3) for the MnO4 oxide, where χM′ is the Mulliken electronegativity of the metal atom and χO is that of the oxygen atom). Therefore, Sanderson’s electronegativity of O=Mn(O)3 is 5.96 eV and that of O=Mn(O)(OH)2 is 6.82 eV.70 Note that the oxygens in the brackets are lattice oxygens and are shared by three metal ions. The electronegativity of Co(O)3(OH)3 side is 6.98 eV [calculated from (χCo2O3X3O8)1/3], where XCoO, is 4.30 eV, X3O8 is 7.54 eV, and X3O8 is 7.18 eV and higher than that of Mn(IV) (O=Mn(O)(OH)2) species; therefore, it may require higher potential to oxidize compared to that of Mn4+ species over the electrode surface (electronegativity difference of at least 160 meV) to Mn3+. To clarify the above statements, we also show the 3D structure of the likely neutral, metal surface species in Figure S22. The electronegativity difference in both NiCo2O4 and ZnCo2O4 cases (O=Co(O)3(OH)3, 6.93 eV, versus Ni(O)3(OH)2, 6.99 eV, and O=Co(O)3(OH)2 versus Co(O)3(OH)2, respectively) is only 60 and 50 meV,
respectively. This difference could be further reduced in m-ZnCo2O4 due to the Zn(II) ion, which is the most electro-negative atom among all the four metals (χ values of Mn, Co, Ni, and Zn are 3.72, 4.30, 4.40, and 4.48 eV, respectively). Therefore, step 3 in our previous proposal may occur at a lower potential and may be considered as a second step rather than a third step. The corrected new mechanism is shown in Figure 10a. Also note that manganese can be oxidized to +5 or higher oxidation states and increases the rate of the chemical reaction (attack of hydroxide to oxygen-oxygen over the surface to form the O–O bond) in the second step and may be eliminated being part of the slow step in the OER to contribute to A2. However, in cobalt-modified LiMn2−xCoO4, m-NiCo2O4, and m-ZnCo2O4, the Co(IV) sides (tetrahedral Co(O)3O or octahedral O=Co(O)3(OH)2, see Figure 10a, step 2) are the active sides and are neutral, which may slow the chemical reaction and make it part of the rate-determining step. However, in LiMn2O4 and m-MnCo2O4 (especially at higher calcination temperatures), the active sites are tetrahedral or octahedral manganese oxo and manganese oxo/cobalt oxo, respectively, over the electrode surface and influence the reaction mechanism of the OER process. Therefore, it is reasonable to suggest that the OER mechanism is changed or slightly modified in the m-MnCo2O4 electrodes.

## CONCLUSIONS

Two salt couples, namely, Mn(II)/Co(II), Ni(II)/Co(II), and Zn(II)/Co(II) nitrates, form a liquid crystalline mesophase with C12E10 and P123 in a broad range of salt/surfactant mole ratios in the presence of a charged surfactant, CTAB. CTAB stabilizes the LLCM at extremely high salt concentrations. The salt/C12E10 mole ratio can be as high as 25, but the mesophases are stable up to mole ratios of 8 and they leach out salt species at higher concentrations. The mesophases above mole ratios of 10 are metastable but can be prepared as fresh solutions and then upon coating over a substrate may be calcined immediately to form mesoporous metal cobaltites. Mesophases at 10 mole ratio of salts/C12E10 and 60 mole ratio of salts/P123 are stable long enough to be prepared as thin gel films that can be calcined to form smooth thin films of metal cobaltites (MCO3O4, where M is Mn, Ni, and Zn). All three metal cobaltites form nano-crystalline pore walls at temperatures as low as 250 °C; however, efficient surfactant burning occurs over 300 °C. The pore walls are constructed from crystalline MCO3O4 nanoparticles that grow by annealing or directly calcining the films at higher temperatures, but MnCo3O4 resists high temperatures up to 550 °C. Both MnCo3O4 and ZnCo3O4 films are pure without another crystalline phase; however, NiCo3O4 contains a NiO phase at elevated temperatures. The pore size, in both NiCo3O4 and ZnCo3O4 films, expands with increasing calcination/annealing temperatures, but the pores are more uniform with a smaller pore-size distribution in the MnCo3O4 films. The mesoporous MCO3O4 film can also be fabricated over FTO glasses and used as a WE in an alkaline solution for the OER. Typical CV curves of MnCo3O4 and NiCo3O4 display oxidation peaks due to manganese and cobalt and nickel and cobalt species, respectively, but the CV curve of ZnCo3O4 consists of a reversible peak due to oxidation/reduction of the Co3+/Co4+ couple, which is the only electroactive side for the OER process. The m-NiCo3O4 and m-ZnCo3O4 electrodes display similar Tafel slopes (around 60 mV/dec). Overpotentials, required for the whole m-MC3O4 electrodes, occur around 200 mV at 1 mA/cm² current density. This increases incrementally with increasing current density; however, the major overpotential is due to the high resistance (mostly originated from the FTO substrate) of the electrodes. This may be compensated by using a more conductive substrate in the fabrication of the electrodes. All electrodes are stable under harsh OER conditions with little change in both m-MnCo3O4 and m-ZnCo3O4 electrodes and a significant but positive change in the m-NiCo3O4 electrode. The m-NiCo3O4 electrodes become better conductors over time in the long-run CP experiments. The OER mechanism is similar in m-NiCo3O4 and m-ZnCo3O4 electrodes but differs in the m-MnCo3O4 electrode. Changes in the mechanism may be related to the electronegativity of the surface species, such that manganese needs to be at the +5 oxidation state for the OER process, and the positively charged Mn5+ side enhances the hydroxide concentration around the manganese-oxo side and increases the rate of hydroxide attack to the manganese-oxo side for the O–O bond formation, immediately after the first electron transfer. This eliminates the slow chemical step (attack of hydroxide to metal-oxo) from being part of the rate-determining step in the OER of the m-NiCo3O4 and m-ZnCo3O4 electrodes. Factors for producing efficient electrodes include the electrode stability, surface area, surface chemical composition, and crystallinity of the pore walls, and the m-MCO3O4 thin-film electrodes satisfy all the abovementioned factors. Therefore, this research can be expanded along these lines by modifying the MASA process using other transition-metal salts and/or polymerizing ingredients (such as tetraethyl-borosilicate) and surface modification techniques.

## ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.1c00064.

Additional XPS spectra, small- and high-angle diffraction patterns, N2 adsorption–desorption data, SEM and TEM images, electrochemical data including CV curves, CPs, IV, and Tafel plots, and the content of solutions used in the synthesis (PDF)

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ABBREVIATIONS
MASA, molten salt-assisted self-assembly; OER, oxygen evolution reaction; CP, chronopotentiometry; CA, chronoamperometry; BET, Brunauer–Emmett–Teller; BJH, Barrett–Joyner–Halenda.

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