FeCo\textsubscript{1.6}Mn\textsubscript{0.4}O\textsubscript{4} microspheres as catalysts for oxygen reduction reaction

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Abstract. The representative spinel-type materials AB\textsubscript{2}O\textsubscript{4} (Both of A and B are transition metals) electrocatalysts for oxygen reduction reaction (ORR) have been investigated widely. But FeCo\textsubscript{2}O\textsubscript{4} was not explored widely as the ORR electrocatalyst. The element of B site in AB\textsubscript{2}O\textsubscript{4} had a determined influence on the electrochemical performance of the sample according to the previous research. In this work, a part of Co element at B site in FeCo\textsubscript{2}O\textsubscript{4} was doped by Mn to improve the electrochemical performance for the popular research. FeCo\textsubscript{1.6}Mn\textsubscript{0.4}O\textsubscript{4} microspheres were prepared and characterized with XRD, SEM, XPS. The electrochemical performances were tested and the results were analyzed. Meanwhile, the stability and methanol tolerance ability of catalysts were also measured. The work found a superior performance and non-precious catalyst for oxygen reduction reaction.

1. Introduction
In recent years, the development of Li-ion Batteries and regenerative fuel cells in portable mobile devices increased fast. Fuel cells attract much attention due to its environment-friendly properties. But the sluggish kinetics of cathodic oxygen reduction reaction (ORR) significantly restricts the performance and electrochemical behavior of the catalysts. Pt has the superior ORR ability, but the scarcity and high cost make it can’t be used widely. So, the exploration of catalysts with good ORR performance and low-cost is a hot research problem [1-3].

The AB\textsubscript{2}O\textsubscript{4} spinel-type cobalt oxides are oxides which have various properties like ORR property, OER property and magnetic property. These spinel-based catalysts provide the advantages over those precious metal-based catalysts from the aspects of the scarce resource, low-cost, stability [4-6]. But FeCo\textsubscript{2}O\textsubscript{4} was not explored widely like ZnCo\textsubscript{2}O\textsubscript{4} (or NiCo\textsubscript{2}O\textsubscript{4}) as the ORR electrocatalyst for its ordinary performances. Mn is a kind of transition metal element with different valence states and it shows superior performance in the electrochemical area. Doping is an efficient way to improve the performance of material due to the change of crystal structure [7-9]. The Mn-doped FeCo\textsubscript{2}O\textsubscript{4} has the potential of being a candidate of Pt-based ORR catalyst.
In this work, the Mn-doped FeCo$_2$O$_4$ microspheres were synthesized with the hydrothermal method. We demonstrated the feasibility of improved electrocatalytic activities of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ with the help of the thin-film RDE technique. The micromorphology characteristics of the prepared samples were identified via X-ray diffraction (XRD), Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS). After a series of electrochemical tests, the FeCo$_{1.6}$Mn$_{0.4}$O$_4$ showed an enhanced ORR catalytic activity than FeCo$_2$O$_4$ and acceptable stability, which indicated the potential of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ as the candidate of the commercial Pt/C.

2. Material Synthesis

The FeCo$_{1.6}$Mn$_{0.4}$O$_4$ microspheres were prepared by the two-step method. The method is as follows: (1) synthesis of the precursors: 5 mmol of Fe(NO$_3$)$_2$·9H$_2$O, 8 mmol of Co(NO$_3$)$_2$·6H$_2$O and 2 mmol of MnCl$_2$·4H$_2$O were dissolved into 150ml ethylene glycol (EG) completely. After that, 90 mmol of urea was added with vigorous stirring for 1h. Then transferred the solution to a Teflon-lined stainless-steel autoclave with a capacity of 50 mL for hydrothermal treatment at 180 °C for 12h. The precipitate was collected by centrifugation and washed with ethanol several times. Next, the precursor was dried under vacuum at 80 °C for 12 h. (2) Synthesis of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ microspheres: The precursor was calcined at the temperature of 500 °C for 3 h with a temperature ramp of 2.5 °C/min to collect the sample.

The FeCo$_2$O$_4$ microparticles were synthesized for reference. 1 mmol Fe(NO$_3$)$_2$·9H$_2$O and 2 mmol Co (NO$_3$)$_2$·6H$_2$O were dissolved in distilled water. Then, 9 mmol citric acids were added into the above solvent with continuously stirring to ensure the agent dissolved completely. The solution was heated with 90°C until the formation of gel and the gel was dried in the oven at 120 °C for overnight. At last, the precursor was pressed into a pill with the calcining treatment of 500 °C for 3 h to get the sample.

3. Characterization

The crystal structure of the samples was characterized by powder x-ray diffraction. The morphological and size analyses were visually measured via a field scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) measurement was carried out to obtain the chemical composition and the chemical bonding state of prepared samples.

The FeCo$_2$O$_4$ main diffraction angles at 18.5°, 30.6°, 36.1°, 43.9°, 54.4°, 58.1°, 63.8°, 75.6° are corresponding to the crystal plane of (111), (220), (311), (400), (422), (511), (440) and (533) respectively in Figure 1. The diffraction peaks of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ show a weak shift due to the small dose doping of Mn. The XRD patterns show no other impurities peaks in the FeCo$_2$O$_4$ and FeCo$_{1.6}$Mn$_{0.4}$O$_4$, which indicates the high purity of the obtained samples.

As Figure 2(a) shows, the prepared FeCo$_2$O$_4$ microparticles are not regular microstructure and the size is about 1 um. The synthesized FeCo$_{1.6}$Mn$_{0.4}$O$_4$ in Figure 2(b) and Figure 2(c) show the microspheres with the size of 2 um and a tough structure of the surface. The morphology of microsphere provides the sample with a higher specific surface area in the reaction process, which is
important for the enhancement of the ORR catalytic activity. The prepared samples are further analysed by EDS in Figure 2(d). The elements of Fe, Co, Mn, O can be seen clearly and the atomic ratios of Fe: Co: Mn in the inset of Figure 2(d) is close to the presumed stoichiometric ratios of Mn=0.4, which indicates the successful preparation of FeCo1.6Mn0.4O4.

Figure 2. SEM image of FeCo1.6O4 (a); SEM image of FeCo1.6Mn0.4O4 microspheres (b); SEM image of the magnifying FeCo1.6Mn0.4O4 microsphere (c); EDS image of FeCo1.6Mn0.4O4 microspheres (d).

The typical survey XPS spectrum in Figure 3(a) shows the existence of Fe, Co and Mn elements in FeCo1.6Mn0.4O4. The map of Fe element shown in Figure 3(b) describes the peaks for Fe 2p1/2 at 723.2 eV and Fe 2p1/2 at 710.1 eV, respectively. The valence of Fe cation is analysed to be 3+ due to the oxidation of Co3+. Figure 3(c) shows the map of Fe cation. The peaks at 796.2 eV and 781.3 eV are ascribed to Co2+, and the peaks at 794.8 eV and 779.6 eV are ascribed to Co3+, respectively. Figure 3(d) reveals the spectrum of Mn 2p. The peaks of which at 654.4 eV and 643.4 eV are ascribed to Mn2+ and
the peaks at 653.3 eV and 641.6 eV are ascribed to Mn$^{3+}$ respectively according to the fitted curves. The results indicate the valences distribution that the Co$^{2+}$ and Mn$^{2+}$ occupy the A site and the Co$^{3+}$, Mn$^{3+}$, Fe$^{3+}$ occupy the B site in the AB$_2$O$_4$ spinel-type oxide, respectively, which implies active catalytic activity.

4. Electrochemical measurements

Electrochemical behaviours of the prepared materials FeCo$_{1.6}$Mn$_{0.4}$O$_4$ were researched by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). Chronoamperometry was used to test the stability and methanol tolerance performances. All of the measurements were carried out in 0.1 M KOH solution.

The CV curves in N$_2$-saturated (dash line) and O$_2$-saturated (solid line) solution are shown in Figure 4(a). The O$_2$-saturated curve of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ shows a distinct oxygen reduction peak at 0.58 V and a decrease of current could be seen at the potential of about 0.8 V but no obvious reduction peak and current decay in N$_2$-saturated solution, which indicates the possibility of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ for the oxygen reduction reaction.

The ORR kinetics on FeCo$_{1.6}$Mn$_{0.4}$O$_4$, FeCo$_2$O$_4$ and Pt/C (20 wt. %) in O$_2$-saturated solution are measured to get the further electrochemical performance. As shown in Figure 4(b), the onset potential of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ is 0.85 V and the onset potential of FeCo$_2$O$_4$ is about 0.72 V. The FeCo$_{1.6}$Mn$_{0.4}$O$_4$ exhibits a more positive potential of 0.13 V and a much higher diffusion limiting current density than FeCo$_2$O$_4$, which shows the enhancement of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ for ORR catalytic activity. In addition, the onset potential of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ is about 122 mV lower than Pt/C (20 wt. %) and the difference of half-wave potential between them is small. The comparison of the samples indicates the acceptable ORR activity of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ and the potential of being a candidate for non-noble ORR catalyst.

The polarization curves of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ for the ORR (at rotation rates of 400 rpm–2000 rpm) and the corresponding Koutecky-Levich (K-L) plots are shown in Figure 4(c) and Figure 4(d), respectively. The diffusion limiting current densities are increased with the rise of the rotation rates from Fig. 4(c). The direct four pathway of ORR process in alkaline solution is shown as the following reaction [10-11]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

The Koutecky-Levich model is applied to address the ORR process quantitatively and it can be used to calculate electron transfer numbers. The ORR kinetic parameters of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ ($n$ value) was analysed by using the following Koutecky-Levich model based on the LSV test result ( $i$ is the measured current density, $i_K$ is the kinetic current density and $\omega$ is the rotation speed (rpm), respectively. $B$ stands for the Koutecky-Levich slope.)

$$\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_\omega} = \frac{1}{i_K} + \frac{1}{B\omega^{3/2}}$$

The theoretical value of $B$ is evaluated by the following equation:

$$B = 0.2 \times n \times F \times C_{O_2} \times D_{O_2}^{2/3} \times \nu^{-1/6}$$

$n$ is the transferred electron number; $F$ is Faraday constant (9.6485 C mol$^{-1}$), $D_{O_2}$ is the diffusion coefficient of O$_2$ ($D_{O_2} = 1.86 \times 10^{-5}$ cm$^2$s$^{-1}$), $\nu$ is the kinetic viscosity of the solution ($\nu=0.01$ cm$^2$ s$^{-1}$), $C_{O_2}$ is the concentration of O$_2$ dissolved in electrolyte ($C_{O_2} = 1.21 \times 10^{-6}$ mol cm$^{-3}$) [12-14].

As shown in Figure 4(d), the Koutecky-Levich plots at various potentials exhibit good linearity and near gradient, suggesting similar electron transfer numbers for ORR at different potentials. The average transferred electron is 3.85, suggesting that the four-electron pathway is dominant on the ORR process of FeCo$_{1.6}$Mn$_{0.4}$O$_4$. 


Figure 4. CV curves of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ as ORR catalysts in O$_2$-saturated (blue line) and N$_2$-saturated (black line) (a); The comparison of ORR polarization curves of FeCo$_2$O$_4$, FeCo$_{1.6}$Mn$_{0.4}$O$_4$ microspheres and Pt/C at 1600 rpm (b); LSVs of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ at different rotation rates with a sweep rate of 5 mV s$^{-1}$ (c); Koutecky-Levich (K-L) plots at different electrode potentials for FeCo$_{1.6}$Mn$_{0.4}$O$_4$ (d).

The chronoamperometric method is applied to examine the stability of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ towards ORR in O$_2$-saturated 0.1 M KOH at a rotation speed of 1600 rpm. The Pt/C is also measured for comparison. As shown in Figure 5(a), both of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ and Pt/C shows the same decay of about 9.4% after 10000 s. But FeCo$_{1.6}$Mn$_{0.4}$O$_4$ exhibits a more stable change. The methanol tolerance ability of catalysts is a very important factor that influences the application of materials in the commercial field. The methanol tolerance ability measurements of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ and Pt/C are shown in Figure 5(b). The change of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ curve is tiny compared with that of Pt/C after the addition of 3M methanol, which indicates the better methanol tolerance ability of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ than Pt/C. Therefore, the FeCo$_{1.6}$Mn$_{0.4}$O$_4$ has acceptable durability and more excellent methanol tolerance ability than the commercial Pt/C as ORR catalyst, which makes it be a low-cost and desirable succedaneum in the field of fuel cell and rechargeable devices.

Figure 5. 10,000 s chronoamperometry test (0.6 V vs. RHE) of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ microspheres catalyst, and 20% Pt/C catalyst at 1600 rpm (a); The chronoamperometric response (0.6V vs. RHE) of FeCo$_{1.6}$Mn$_{0.4}$O$_4$ microspheres and Pt/C (3 M methanol was added after 1800 s) at 1600 rpm (b).
5. Conclusion
The work introduced a kind of Mn-doped spinel microspheres for ORR catalyst and the microsphere structure was synthesized by hydrothermal method. The measured electrochemical performances results of the prepared FeCo$_{1.6}$Mn$_{0.4}$O$_4$ demonstrated the good ORR catalytic activity. The work found a spinel-type FeCo$_{1.6}$Mn$_{0.4}$O$_4$ to be a candidate of Pt-based noble catalysts.

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References
[1] Han, S., Liu, S.Q., Yin, S.J., Chen, L., He, Z. (2016) Electrodeposited Co-Doped Fe$_3$O$_4$ Thin Films as Efficient Catalysts for the Oxygen Evolution Reaction. Electrochimica Acta, 210: 942-949.
[2] An, B., Mo, Y., Guo, L., et al. (2014) A novel porous coral-like Zn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$ as an anode material for lithium ion batteries with excellent rate performance. Journal of Power Sources, 269(4): 795-803.
[3] Cao, Y., Cai, S.R., Fan, S.C., et al. (2014) Reduced graphene oxide anchoring CoFe$_2$O$_4$ nanoparticles as an effective catalyst for non-aqueous lithium-oxygen batteries. Faraday Discussions, 172: 215-221.
[4] Hu, L., Huang, Y., Chen, Q. (2013) Fe$_x$Co$_{3-x}$O$_4$ nanoporous particles stemmed from metal-organic frameworks Fe$_3$[Co(CN)$_6$]: A highly efficient material for removal of organic dyes from water. Cheminform, 559(25): 57-63.
[5] Laouini, E., Berghoute, Y., Douch, J., et al. (2009) Electrochemical behaviour of Fe$_x$Co$_3$O$_4$ with (x=0, 1, 2 and 3) oxides thin film electrodes in alkaline medium. Journal of Applied Electrochemistry, 39(12): 2469-2479.
[6] Kim, H., Seo, D.H., Kim, H., et al. (2012) Multicomponent Effects on the Crystal Structures and Electrochemical Properties of Spinel-Structured M$_2$O$_4$ (M = Fe, Mn, Co) Anodes in Lithium Rechargeable Batteries. Chemistry of Materials, 24(4): 720-725.
[7] Mary, A.J.C., Bose, A.C. (2017) Hydrothermal synthesis of Mn-doped ZnCo$_2$O$_4$ electrode material for high-performance supercapacitor. Applied Surface Science, 425.
[8] Yu, M., Chen, J., Ma, Y., et al. (2014) Hydrothermal synthesis of NiCo$_2$O$_4$ nanowires/nitrogen-doped graphene for high-performance supercapacitor. Applied Surface Science, 314: 1000-1006.
[9] Shang, X., Yan, K.L., Lu, S.S., et al. (2017) Controlling electrodeposited ultrathin amorphous Fe hydroxides film on V-doped nickel sulfide nanowires as efficient electrocatalyst for water oxidation. Journal of Power Sources, 363: 44-53.
[10] Liu, K., Li, X., Liang, L., et al. (2018) Ni-doped ZnCo$_2$O$_4$, atomic layers to boost the selectivity in solar-driven reduction of CO$_2$. Nano Research, 11(6): 2897-2908.
[11] Zhao, Y., Zhou, X., Yong, D., et al. (2016) A study of photocatalytic, chemical, and electrocatalytic water oxidation on AC$_2$O$_4$ (A = Ni, Cu, Zn) samples through doping different metal ions. Journal of Catalysis, 338: 30-37.
[12] Yan, W., Yang, Z., Bian, W., et al. (2015) FeCo$_2$O$_4$/hollow graphene spheres hybrid with enhanced electrocatalytic activities for oxygen reduction and oxygen evolution reaction. Carbon, 92: 74-83.
[13] Bian, W., Yang, Z., Strasser, P., et al. (2014) A CoFe$_2$O$_4$/graphene nanohybrid as an efficient bifunctional electrocatalyst for oxygen reduction and oxygen evolution. Journal of Power Sources, 250: 196-203.
[14] Ratha, S., Samantara, A.K., Rout, C.S., et al. (2015) Synergistic Electrocatalytic Activity of Spinel ZnCo$_2$O$_4$/Reduced Graphene Oxide Hybrid towards Oxygen Reduction Reaction. Journal of Solid State Electrochemistry, 20(1): 285-291.