Micro Emulsion Synthesis of LaCoO_3 Nanoparticles and their Electrochemical Catalytic Activity

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ABSTRACT

The micro emulsion method has been successfully used for preparing perovskite LaCoO_3 with uniform, fine-shaped nanoparticles showing high activity as electro catalysts in oxygen reduction reactions (ORRs). They are, therefore, promising candidates for the air-cathode in metal-air rechargeable batteries. Since the activity of a catalyst is highly dependent on its specific surface area, nanoparticles of the perovskite catalyst are desirable for catalyzing both oxygen reduction and evolution reactions. Herein, LaCoO_3 powder was also prepared by sol-gel method for comparison, with a broad particle distribution and high agglomeration. The electro catalytic properties of LaCoO_3 and LaCoO_3 -carbon Super P mixture layers toward the ORR were studied comparatively using the rotating disk electrode technique in 0.1 M KOH electrolyte to elucidate the effect of carbon Super P. Koutecky-Levich theory was applied to acquire the overall electron transfer number (n) during the ORR, calculated to be ~ 3.74 for the LaCoO_3 -Super P mixture, quite close to the theoretical value (4.0), and ~ 2.7 for carbon-free LaCoO_3 . A synergistic effect toward the ORR is observed when carbon is present in the LaCoO_3 layer. Carbon is assumed to be more than an additive, enhancing the electronic conductivity of the oxide catalyst. It is suggested that ORRs, catalyzed by the LaCoO_3 -Super P mixture, are dominated by a 2+2-electron transfer pathway to form the final, hydroxyl ion product.

Keywords : Rotating disk electrode, Perovskite oxide, Oxygen reduction reaction, Oxygen evolution reaction, Micro emulsion

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1. Introduction

Transition-metal oxides with perovskite-type structures have received great attention because of their excellent physical properties and potential applications. It is well known that perovskite materials have wide applications in catalysis because of their defective structures and excellent oxygen mobility [1-5]. However, the major drawback of using perovskites as

electro catalysts is their low specific surface area owing to the high temperature required for perovskite phase crystallization [5]. The synthetic method and conditions have been observed to have a strong influence on the catalytic activities of perovskites [6,7]. LaCoO_3 has many practical applications owing to its excellent physical and chemical properties. Synthesis of LaCoO_3 has been achieved with a number of methods, including a sol-gel method [8,9], a poly-

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merizable complex method [10], combustion synthesis [11], molten chloride flux [12], mechanochemical synthesis [13], alkaline co-precipitation [14], and electrochemical oxidation [15]. The properties of the final materials obtained are highly dependent on the preparation method [12-16]. The reverse micro emulsion, which is also known as W/O (water in oil) micro emulsion method, is a recently developed technique, ideal for the preparation of inorganic nanoparticles [17]. Water in oil micro emulsion proceeds by dispersing water phase (dispersion phase) in oil (continuous phase). Oil phase goes to micelles formation on addition of surfactant while water phase containing reactants goes inside the micelles on mixing these two phases. Further mixing results in nucleating the nanoparticles via exchanging the counter ions at the interface between micelles and water. This exchange process is the rate determining step. The micelles act as nano reactors as growth of particle is being progressed inside them. The surfactant nature, water to surfactant ratio, solvent: Oil and reducing agent to surfactant ratio control the final particle size. When water ratio is lowered it result in rigidity, i.e., low mixing of reactants and hence slow growth. While, increasing water ratio leads to better solvation and good inter-micellar exchange rate which results in decrease in particle size. Hence, optimum water to surfactant ratio is used. Solvent affect particle growth rate and final product size. When the solvent having smaller molecular volumes were used, they penetrate into the tails of surfactant giving rigidity and slow growth rate. So, keeping this effect in mind, Isooctane which is somehow bulky and have larger molecular volume were used to control loose penetration at the tails of surfactant and increasing growth rate to control crystallites size [18]. The main advantages of this approach are that the reactants are mixed at a more homogeneous level in this oil-based solution, and grains are effectively inhibited from coalescing during the synthetic process. The final materials have superior properties; including nanometric dimension grain sizes, uniform size distribution, and phase purity [19].

Oxygen reduction and oxygen evolution are essential electrochemical reactions in rechargeable metal–air batteries, fuel cells, chloralkali cells, water electrolyzers, and CO₂ reduction. Rechargeable metal–air batteries generate electricity through a redox reaction between the metal and oxygen in the air. Alkaline solutions are commonly used as electrolytes in aqueous metal–air batteries. In aqueous electrolytes, metal–air batteries encounter large discharge-charge over potentials (i.e., large voltage gaps and low round-trip efficiency), arising from slow rates of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) in the absence of catalysts. The presence of an oxygen electro catalyst can accelerate the ORR and OER processes [20, 21]. Noble metals such as Pt (performs poorly in OER) and noble metal oxides such as IrO₂ or RuO₂ (performs poorly in ORR) are used as state-of-the-art electro catalysts for ORR and OER, respectively [21, 22]. However, noble metals are expensive, and hence, research efforts are focused on developing low-cost transition-metal oxides as alternative electro catalysts. Metal oxide catalysts incorporated into the carbon electrode enhance both oxygen reduction and evolution kinetics, and increase the specific capacity of the cathode [23]. Shao-Horn and co-workers have intensively studied perovskite oxides with the help of molecular orbital principles, and showed that LaCoO₃ is one of the promising candidates among the various perovskite-type oxides, possessing distinctive intrinsic activity for both ORR and OER [24]. However, despite numerous studies, the exact mechanism of ORR on perovskites is still unclear. Both direct 4e[−] [24] and series 2e[−] + 2e[−] pathways [25] have been proposed for perovskite cathodes. The reactions at the alkaline electrolyte can be written, as shown in Table 1.

However, mass-transport resistance and/or incomplete wetting of the electrode structure often hamper the evaluation of the intrinsic electro catalytic activity of catalysts. It is proposed that the use of rotating disk electrode (RDE) measurements, a fast screening tool with well-known mass-transport properties where the

Table 1. Different pathways for reactions in alkaline electrolyte

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	4-electron pathway
(i) $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	2+2-electron pathway
(ii) $HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$ or $H_2O_2 \rightarrow O_2 + H_2O$	

electro catalyst and Nafion solution are deposited onto a glassy carbon (GC) RDE, would help avoid or reduce these problems [26]. When an electrode is rotated, the mass transfer of reactants and products occurs by a convective-diffusional mechanism. The theory of convective flow at the RDE is identical to the theory of flowing fluids (hydrodynamics) [27], and is thus termed hydrodynamic voltammetry. At the RDE, a hydrodynamic flow pattern results from centrifugal forces that move the liquid horizontally out and away from the center of the disk while fresh solution continually replaces it with the flow normal to the electrode surface.

It has been demonstrated that perovskites alone show low electro catalytic activity, which may be increased by a few orders of magnitude when carbon is added to the catalytic layer. There is a synergistic chemical coupling between perovskite and carbon [28]. In this study, a thin-film RDE technique was used, whereby a very thin layer of LaCoO_3 electro catalyst, synthesized by the micro emulsion method, was tested in order to reveal the influence of carbon super P on the catalytic activity of the LaCoO_3 electro catalyst.

2. Experimental

2.1 Material synthesis & characterization

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (98.0%) and citric acid (~99.5%) were purchased from Samchun. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>98%), Hexadecyltrimethylammonium bromide (CTAB) (>99%), 2, 2, 4-Trimethylpentane/Isooctane (reagent grade), and 1-pentanol (reagent grade) were obtained from Sigma-Aldrich (St. Louis, MO, USA). KOH was supplied by Kanto Chemical. Individual aqueous solutions of metal nitrates ([Co/La] nominal = 1) were mixed together thoroughly. Citric acid was added as the complexing agent to the above solution. The molar ratio of cations to citric acid was 1:1. Excess water was evaporated under slow stirring at 343 K. The obtained viscous gel was then vacuum dried at 393 K. The spongy material obtained was crushed and calcined at 923 K for 3 h in an open furnace, and the product designated as “LCO-SP.”

For the synthesis of LaCoO_3 via the micro emulsion method, 1-pentanol (6 mL) was added to 2, 2, 4-trimethylpentane (30 mL), followed by the addition of CTAB (6.0 g). The mixture was stirred at ambient temperature until no bulk particles remained. Two

portions of the micro emulsion solution were taken, marked A and B, respectively. KOH aqueous solution (5.5 mL, 1 M) was injected into A. La-nitrate solution (2 mL, 0.5 M) and Co-nitrate solution (2 mL, 0.5 M) were mixed and injected into B. Both A and B were stirred until the solutions became clear. Equal portions of A and B were then mixed together, followed first by vigorous stirring, and then slow stirring for 6h at ambient temperature. The resulting product was collected by centrifugation, washed with ethanol and water, and then calcined at 923 K for 3 h in an open furnace. The product was designated as “LCO-ME.”

The calcined samples structures were characterized by X-ray diffraction (XRD) using a Rigaku X-ray diffractometer equipped with $\text{Cu-K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. The diffraction angle (2θ) ranged between 10° and 80° . The particle size and morphology of the samples were characterized with a field emission scanning electron microscope (FE-SEM; Hitachi, S-4200). N_2 adsorption and desorption isotherms were measured at 77.35 K using a Micromeritics ASAP 2020 Gas Adsorption Analyzer. The pore size distribution was determined from analysis of the desorption branch of the N_2 isotherm using the BJH (Barrett-Joyner-Halenda) method.

3.3 Oxide electrode preparation

The perovskite oxide powder was mixed with carbon (Super P) at a 5:1 mass ratio of oxide to carbon in order to remove any electronic conductivity limitations in the thin-film electrodes. The carbon was used as received. The electro catalyst suspension was prepared by sonication (UIL-15040 sonicator) of perovskite oxide (5 mg) and the above mentioned oxide-carbon mixture (1 mg) in tetrahydrofuran (THF, 1 mL) for 20 min. THF is preferable to solvents such as acetone, ethanol, and water, as it allows stable dispersion of oxide powder in the suspension [23]. The GC disk electrode was prepared by polishing with $0.05 \mu\text{m}$ alumina slurry on a clean polishing cloth (Buehler) until a mirror-like surface was obtained, and then sequentially rinsed with distilled water and ethanol, and dried with a lint-free tissue paper. A $3 \mu\text{L}$ aliquot of the resultant suspension was drop-casted onto the GC disk electrode (3 mm diameter, 0.0707 cm^2 area, RRDE-3A, ALS). After slow evaporation of the solvent, $1 \mu\text{L}$ of Nafion solution (5 wt.%, Fluka) was drop-casted on the electrode sur-

face and left to dry slowly overnight inside a closed beaker to allow the catalyst particles to attach to the GC disk electrode.

3.4 Electrochemical measurement

The RDE measurement system in an aqueous electrolyte included a platinum counter electrode, an Ag|AgCl (3M NaCl) reference electrode (RE-1B, ALS, Japan), and a thin-film working electrode (coated on a GC disk). Voltammetric experiments were performed with a Biologic VMP3 multichannel potentiostat. Cyclic voltammetry (CV) and linear scanning voltammetry (LSV) were conducted in 0.1 M KOH solution electrolyte prepared from deionized water and KOH pellets (99.99%). The GC electrode loaded with the catalyst was immersed in the (argon) Ar -purged electrolyte for at least 30 min prior to study. After steady-state CVs were obtained in nitrogen, the O₂ gas supply line was purged for another 30 min. After pre-cycling, the ORR polarization curve was tested from 0.2 V to -0.52 V followed by a voltage scan from 0 V to 0.7 V to examine the OER polarization curve. All potentials in this study were relative to the Ag|AgCl (3 M NaCl) reference electrode.

3. Results and Discussion

Powder XRD data (Fig. 1) shows the as-synthesized perovskite oxides LCO-ME and LCO-SP obtained from the micro emulsion and sol-gel methods, respectively. XRD patterns of both samples

Fig. 1. XRD patterns of two LaCoO₃ samples prepared by sol-gel (LCO-SP) and micro emulsion (LCO-ME) methods.

exhibited diffraction peaks consistent with those of LaCoO₃ (JCPDS No.-01-084-0848), irrespective of the preparation method. This showed that highly crystalline phases formed due to well-mixed cations in the hydrolysis and condensation steps of sol-gel synthesis and the nucleation and growth steps in the micro emulsion method. XRD patterns of both samples presented strong reflections at 32.9° (110) and 33.3° (104), corresponding to hexagonal crystal symmetry with an R3c space group. XRD results showed no trace of hexagonal La(OH)₃, corresponding to the 2θ values 27.3° (110), 28.0° (101), and 39.5° (201), which indicated the high degree of La and Co oxide incorporation into the perovskite structure achieved by both methods. The lattice parameters calculated from these XRD patterns are shown in Table 2. The lattice parameters and cell volumes of the perovskite phase were almost similar for both samples and in agreement with the literature [29]. The crystallite size was estimated using the Scherrer formula ($D = 0.9\lambda/\beta \cos\theta$, where d , λ , θ , and β are the crystallite size, X-ray wavelength (1.5418 Å), Bragg diffraction angle, and full width of the half maximum (FWHM) of the diffraction peak, respectively). Crystallite sizes of the samples prepared by the two different methods were calculated from the broadening of the (024) reflection of the LaCoO₃ phase at a 2θ angle of 47.5° and are tabulated in Table 2. It was evident from the calculation that LaCoO₃ prepared by the micro emulsion method exhibited the lowest crystallite size (~23 nm) compared to the catalysts prepared by the sol-gel method and calcined at the same temperature (650°C). The larger crystallite size of the LaCoO₃ phase observed in the LCO-SP sample was indicative of the greater growth of its crystal domains. This result reveals that intended for smaller crystallite size mixings of cations by way of nucleation and growth

Table 2. Structure parameters of LaCoO₃ synthesized by two different methods

	Standard	LCO-ME	LCO-SP
<i>a</i> (Å)	5.4425	5.4445	0.5437
<i>b</i> (Å)	5.4425	5.4445	0.5437
<i>c</i> (Å)	13.0929	13.103	13.099
Cell volume (Å ³)	335.86	336.4	335.4
Crystallite size <i>D</i> ₀₂₄ (nm)	-	23	31

Fig. 2. SEM micrographs of two LaCoO_3 samples prepared by (a) sol-gel and (b) microemulsion methods.

Fig. 3. Nitrogen adsorption-desorption isotherm and pore size distribution (inset) of two LaCoO_3 samples prepared, by using (a) sol-gel (LCO-SP) and (b) micro emulsion (LCO-ME) method.

steps is more appropriate over the following sequence such as hydrolysis, condensation, and then densification.

Morphologies of LaCoO_3 synthesized with the sol-gel and micro emulsion methods are presented in Figs. 2(a) and (b), respectively. A comparison of these processes reveals that the micro emulsion method resulted in a more reduced particle size and homogeneity, while the powder prepared by the sol-gel method showed a relatively larger particle size and an irregular shape. The average particle size of LaCoO_3 synthesized by the micro emulsion method is about 100 nm with a spherical shape, whereas that from the sol-gel process has a broader particle size distribution. Thus, SEM results are consistent with the results of crystallite size estimation (see Table 2). Particle size is different from crystallite size. A particle may be made up of several different crystallites. LaCoO_3 synthesized by the micro emulsion method (LCO-ME sample) showed a smaller particle and crystallite size, and hence a higher active surface area than that of the LCO-SP sample. In the sol-gel process, after hydrolysis and condensation the resultant gels have to be densified by thermal treatment. In this

study, the metal-citrate precursor gel was vacuum dried at 393 K for densification. This drying stage is connected to shrinking; this step usually constrains the particle size of the final product [30]. Thus, the nanocrystals possibly aggregated to form the large particle during the drying step, which is uncontrollable. Further heat treatment was applied for driving out the residual organic components and for perovskite phase formation. In contrast, the main strategy for the synthesis of nanoparticles in W/O micro emulsions consists of mixing two micro emulsions, one containing the metallic precursor and the other containing a precipitating agent. Upon mixing, both reactants contact each other due to droplet collisions and coalescence, and react to form precipitates of nanometric size that remain conneed to the interior of micro emulsion droplets. The droplet size is governed by the ratio of water and surfactant [31]. The particles can be made larger by increasing the droplet size. This makes the particles grow within the space hindered by the micelles, offering homogeneous nanoparticle formation [31]. This resulted in smaller crystallites, smaller particle size, and large surface area, affording good electro catalytic proper-

ties. The sample prepared in this study by the micro emulsion method had much narrower particle size distribution (Fig. 2(b)), owing to the isolated conditions used during nucleus formation and the subsequent grain growth for each particle.

The N_2 adsorption desorption isotherm and the corresponding Barrett-Joyner-Halenda (BJH) pore size distributions are depicted in Fig. 3 and corresponding average values regarding specific surface area, pore size and volume are presented in Table 3. Both LCO-SP and LCO-ME samples present typical type-IV N_2 sorption isotherms with distinct H3 hysteresis loops that can linked to slit-shaped pores. The BET surface area of LCO-ME nanoparticles is $19.09 \text{ m}^2 \text{ g}^{-1}$ which is much larger than that of the prepared LCO-SP nanoparticles ($5.49 \text{ m}^2 \text{ g}^{-1}$). The pore-size distribution curve shows porous LCO-ME nanoparticles with an average pore width $\sim 12.39 \text{ nm}$. The single point total pore volume of LCO-SP and LCO-ME are revealed to be 0.016 and $0.061 \text{ cm}^3 \text{ g}^{-1}$, respectively. Based on aforementioned analysis, LaCoO_3 perovskite prepared by micro emulsion method is believed to be a superior catalyst. Increasing number of pores and specific surface area in this sample is possibly able to provide more free channels for oxygen transportation and electrochemical active site for reaction, respectively, during ORR. The results from the above characterization of these materials revealed that it was possible to obtain a perovskite material with a smaller particle size as well as higher surface area and pore volume, with the micro emulsion technique than with sol-gel preparation method. Therefore, reverse micro emulsion method was a suitable route for the preparation of nanometer-sized perovskite-type solids with higher active surface areas.

The ORR and OER activities of nano- LaCoO_3 synthesized by using micro emulsion method (LCO-ME) were tested using RDE measurements. To assess the ORR catalytic activity, the samples were loaded onto GC electrodes for CV in O_2 versus Ar-saturated 0.1 M KOH solution at a scan rate of 5 mVs^{-1} in the potential range -0.6 to 0.1 V . LCO-ME sample with

or without carbon super P, were tested with the same mass loading. Featureless voltammetric responses were observed for both LaCoO_3 and LaCoO_3 -Super P mixture-modified GC electrodes in Ar-saturated solutions within the studied potential range. In contrast, when the electrolyte solution was saturated with oxygen, the reduction current appeared as a well-defined cathodic peak around -0.47 V , suggesting pronounced electro catalytic activity of the LaCoO_3 particle-modified GC electrode in oxygen reduction (Fig. 4). Both LaCoO_3 and the LaCoO_3 -Super P mixture showed certain activity during O_2 reduction in alkaline solution, but the oxygen reduction peak of the latter was more positive. This was probably due to carbon participating in the catalysis of reduction in the latter case [25].

Fig. 5(a) shows linear sweep voltammograms representing the ORR in 0.1 M KOH using a thin film of LaCoO_3 , Super P carbon, and the LaCoO_3 -Super P mixture deposited on the rotating disk working electrode, rotated at 1600 rpm during the experiment. As a control experiment, the Ar-saturated solution displayed no noticeable reduction feature between -0.6 and 0.2 V , as expected due to the absence of oxygen. The GC electrode (the substrate onto which the film

Fig. 4. Cyclic voltammetry curves of LaCoO_3 and the LaCoO_3 -Super P mixture on glassy carbon electrodes in O_2 -saturated or Ar-saturated 0.1 M KOH solution. Catalyst loading is the same in both samples.

Table 3. Surface properties of LaCoO_3 synthesized by two different methods

	LCO-SP (Sol-gel)	LCO-ME (Micro emulsion)
BET ($\text{m}^2 \text{ g}^{-1}$)	5.5	19.1
Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	0.016	0.061
Average pore diameter (nm)	11.16	12.39

Fig. 5. (a) Background (argon-saturated) and oxygen reduction reaction (ORR) polarization curves of thin films of glassy carbon, carbon Super P, LaCoO_3 , and the LaCoO_3 -Super P mixture at 1600 rpm. (b) A magnified portion of panel (a) to pinpoint the onset ORR potentials.

was deposited) in an O_2 -saturated system led to an onset of reduction current at approximately -0.33 V, which increased gradually in the potential window studied (up to -0.6 V), as shown in Fig. 5(a). The observed current, nevertheless, was minor when compared to the observed reduction currents for LaCoO_3 , Super P, and the LaCoO_3 -Super P mixture film-deposited GC electrode, indicating that the three modified electrodes acted as catalysts in ORR. A changing trend, similar to that observed in the CV curves, was also observed in the RDE curves, i.e., a relatively high ORR current appeared over the LCO-Super P mixture. Evidently, using LaCoO_3 without carbon led to a comparatively poor performance relative to even that of carbon Super P; this was probably associated with the nonhomogeneous electron transfer inside the film due to the poor electronic conductivity of perovskite oxides [25]. For comparison, and to clearly display the onset potential, a portion of the graph was magnified and is presented in Fig. 5(b). Remarkably, the LaCoO_3 -Super P mixture showed a much more positive ORR onset potential (0.15 V) than both Super P carbon alone (-0.18 V) and LaCoO_3 (-0.15 V). In particular, the ORR current improved from LaCoO_3 , to Super P, and again to the LaCoO_3 -Super P mixture. Adding carbon to LaCoO_3 , in turn, leads to a better performance than when carbon and LaCoO_3 were used alone. This suggested a synergy between LaCoO_3 and carbon. These synergistic effects are consistent with those reported in the literatures [25,28].

The ORR catalytic activity of LaCoO_3 (LCO-SP) samples which was synthesized by using sol-gel process is also observed by applying RDE measurement following the same recipe as described earlier for

Fig. 6. ORR polarization curves of LaCoO_3 samples prepared by using sol-gel (LCO-SP) and micro emulsion (LCO-ME) method with super P with rotation rate at 1600 rpm.

LaCoO_3 (LCO-ME)-Super P modified GC electrode to compare the different particle effect on the oxygen reduction activity of LaCoO_3 oxide material. For metallic catalysts such as Pt, the increase in electrochemical surface area (ECSA) resulting from size reduction has typically been attributed as the reason for enhanced catalytic activity for the undesired reactions [32]. However, for the oxide material enhanced ORR activity resulting from size reduction has attributed to increased conductivity and an increased number of active sites on the reaction surface [33]. In our sample using micro emulsion method (LCO-ME), the particle size was decreased, but also the internal pore was well-developed than the sample using sol-gel method (LCO-SP). Therefore, the LCO-ME particles have comparatively higher ORR activity as shown in Fig. 6, due to their higher electrochemical catalytic activity.

Fig. 7. Oxygen reduction reaction (ORR) polarization curves of (a) LaCoO₃, (b) Super P, and (c) the LaCoO₃-Super P mixture under different rotating rates. (d) Koutecky-Levich plot based on ORR polarization curves at -0.52 V vs. the Ag|AgCl (3 M NaCl) reference electrode.

Another important parameter characterizing the catalytic performance is the number of electrons (n) exchanged during ORR. Fig. 7(a-c) shows typical ORR current densities as a function of rotation rate. All three sample polarization curves consisted of three ranges at “zero rotation”: the kinetics-controlled range (low current), the mixed kinetics and diffusion-controlled range (middle current), and the diffusion-controlled range (plateau current). However, the diffusion-controlled ORR current gradually diminished upon increasing the rotation rate from 200 to 1600 rpm, following the order Super P < LaCoO₃-Super P mixture < LaCoO₃ (Fig. 5a-c). This behavior could be explained by a larger amount of O₂ being adsorbed in the thin film at lower rotation rates, leading to a more noticeable occurrence of an electro reduction current prior to the electro reduction current of O₂ in the bulk electrolyte [25].

ORR reaction kinetics was examined using the Koutecky-Levich correlation:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} = -\frac{1}{nFAkC^0} - \frac{1}{0.62nFAD_{O_2}^{3/4} \nu^{1/4} C^0 \omega^{1/2}}$$

where i corresponds to the measured current, n is the overall transferred electron number, F is the Faraday constant, C^0 is the saturated concentration of oxygen in 0.1 M KOH solution, A is the geometric area of the electrode, ω is the rotating rate, D_{O_2} is the diffusion coefficient of oxygen, ν is the kinematic viscosity of the solution, and k is the rate constant for oxygen reduction.

ORR can occur by two pathways in an alkaline electrolyte: the first is the direct reduction of O₂ to OH⁻ (via a four-electron transfer), referred to as a “direct” 4e⁻ pathway, and the other is a “series” pathway, involving the reduction of O₂ to HO₂ (via a two-electron transfer). The latter pathway may be followed either by a further 2e⁻-reduction of peroxide, or the chemical disproportionation of peroxide [28]. Koutecky-Levich plots are shown in Fig. 7(d). Based on the average values calculated from different potentials, the overall electron transfer numbers of carbon Super P, LaCoO₃, and the LaCoO₃-Super P mixture were 2.4, 2.7, and 3.67, respectively. The overall electron transfer number of the LaCoO₃-carbon mixture was close to the theoretical value (4.0) for

Fig. 8. Oxygen evolution reaction polarization curves of glassy carbon, carbon Super P, and the LaCoO_3 -Super P mixture in O_2 -saturated aqueous electrolyte, 0.1 M KOH, with a sweep rate of 5 mVs^{-1} .

“direct” ORR in alkaline solution. On the other hand, the overall electron transfer numbers of carbon Super P and LaCoO_3 were close to 2 when used alone.

It seems that carbon in the LaCoO_3 -Super P mixture plays a double role: firstly, by improving the ORR current of the catalytic layer, as shown in Fig. 5(a), and secondly, by acting as a catalyst in the reduction of O_2 to HO_2^- (perhaps further reduced to the LaCoO_3 oxide), explained by an assumed 2+2-electron transfer pathway. Thus, the ORR processes catalyzed by the LaCoO_3 -Super P mixture were assumed to be dominated by a 2+2-electron transfer pathway rather than a 4-electron “direct” pathway to form the final product, OH^- .

The OER polarization curves were also examined in O_2 -saturated 0.1 M KOH from 0 to 0.7 V by the RDE technique with the same electrolyte, working electrode, and scan rate as for ORR (Fig. 8). In particular, the LaCoO_3 -Super P mixture exhibited higher OER currents over the entire potential range compared to carbon Super P and the GC substrate. The OER current of carbon Super P was very low, showing that while carbon can act as a mediocre ORR catalyst, it is not at all effective for OER.

4. Conclusion

We have shown that LaCoO_3 perovskite can be formed at particle sizes of $\sim 100 \text{ nm}$ with a uniform size distribution and phase purity when the perovskite precursor particles are synthesized by the micro emulsion

method. This LaCoO_3 material and its carbon mixture (LaCoO_3 -Super P) were used to prepare electrode layers and the influence of carbon Super P toward the ORR was studied by comparing the ORR catalytic performances of Super P, pure LaCoO_3 , and LaCoO_3 -Super P mixture electrodes. The LaCoO_3 -Super P mixture achieved a superior ORR current and a more positive onset potential toward ORR than that of just Super P or LaCoO_3 alone. A synergistic effect was observed in the LaCoO_3 -Super P mixture; the presence of Super P in this electrode layer was anticipated as a possible reason for its improved ORR catalytic activity. The results obtained in this study support the conclusion that carbon Super P was the primary electro catalyst for the $2e^-$ reduction of oxygen to hydro peroxide ions, which were then further catalytically reduced by LaCoO_3 in a second step. LaCoO_3 synthesized in this study by the micro emulsion method can be used as an excellent electro catalyst material in rechargeable metal-air batteries.

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