Highly Dispersed LaCoO₃ on Carbon Prepared via Low-energy Bead Milling as an Oxygen Reduction Electrocatalyst

Naoki TACHIBANA,^{a,b,*} Hiroki KOBAYASHI,^a
 Shoichi SOMEKAWA,^a and Kengo SHIMANOE^c

^a Tokyo Metropolitan Industrial Technology Research Institute, 2-4-10 Aomi, Koto-ku, Tokyo 135-0064, Japan

^b Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasugakoen, Kasuga, Fukuoka 816-8580, Japan

^c Department of Advanced Materials Science and Engineering, Faculty of Engineering Sciences, Kyushu University, 6-1 Kasugakoen, Kasuga, Fukuoka 816-8580, Japan

* Corresponding author: tachibana.naoki@iri-tokyo.jp

ABSTRACT

In this study, fine dispersion of LaCoO₃ nanoparticles on carbon via low-energy bead milling was attempted. X-ray diffraction and scanning transmission electron microscopy revealed that LaCoO₃ nanoparticle agglomerates formed by high-temperature calcination were broken up by milling with small beads at low rotation rate, while suppressing damage to the crystal structure. The low-energy bead-milled LaCoO₃/carbon exhibited 2.7 times higher kinetic current density for the oxygen reduction at −0.15 V vs. Hg/HgO than as-synthesized LaCoO₃/carbon; this enhancement may be attributed to the enlarged surface area and improved dispersion of the oxide on carbon.

© The Electrochemical Society of Japan, All rights reserved.

Keywords : Perovskite-type Oxide, Bead Mill, Oxygen Reduction

1. Introduction

Perovskite-type oxides are known to be active catalysts for the electrochemical reduction of oxygen.^{1–5} The potentiality of the oxides as low-cost oxygen reduction catalysts was first noted by Meadowcroft.⁵ However, the oxides have shown limited catalytic activity in fuel cell and metal–air battery applications. One disadvantage of the perovskite-type oxide catalysts is that their synthesis is usually performed at high temperatures to form a crystalline structure, resulting in agglomeration of the catalyst nanoparticles. In a typical method, an amorphous citrate or malate precursor (ACP or AMP) containing the constituent metals is synthesized and then calcined at high temperature ($\geq 650^\circ\text{C}$).⁶ Although the resulting perovskite-type oxide consists of fine particles, these particles are usually too agglomerated to be finely dispersed on a carbon support.⁷ A high degree of dispersion is an important requisite for electrocatalysts to display high catalytic performance in oxygen reduction.^{1,8,9} Ultrasonication has been utilized to disperse agglomerated materials.¹⁰ However, in the case of nanoparticles, it is difficult to disperse efficiently by the method because the differences between nanoparticle movements are small owing to the low masses of the nanoparticles.¹¹ Bead milling is widely used in industrial-scale production and disperses many types of agglomerates. Conventional bead mill machines usually use a mesh or slit method for separation of the dispersed particles from the beads; therefore, the bead size limit is above 0.1 mm, which is too large with respect to the size of the nanoparticles and results in supply of too much energy to the dispersion system.¹¹ However, over the past decade, nanomaterials, such as titanium oxide,¹² aluminum oxide,¹³ and carbon nanotube,¹⁴ were successfully dispersed by bead milling using small beads. Unlike the usual bead mill machines, a centrifugal separator is used for bead separation, allowing the utilization of small beads in large-scale production. The use of small beads at low rotation speeds is effective for dispersion, while suppressing damage to the nanomaterials.¹²

We investigated the applicability of low-energy bead milling to the dispersion of perovskite-type oxides by conducting experiments on lanthanum cobaltite, LaCoO₃ (LCO), which was chosen as an example of the simplest perovskite-type oxide. Milled LCO was characterized by X-ray diffraction (XRD) analysis and scanning transmission electron microscopy (STEM). The electrocatalytic activity of LCO/carbon composites for the oxygen reduction reaction was investigated using rotating disk electrode (RDE).

2. Experimental

LCO was synthesized by an AMP method.⁶ In a typical synthesis, 5 mmol of La(NO₃)₃·6H₂O (Kanto Chemical) and 5 mmol of Co(NO₃)₂·6H₂O (Kanto Chemical) were dissolved in distilled water (50 mL). Then, 15 mmol of malic acid (Kishida Chemical) was added to the mixture. The mixed solution of malic acid and metal nitrates was adjusted pH to 2.7 by the addition of aqueous ammonia (28%, Wako Pure Chemical). The starting solution was evaporated to dry powder, followed by calcination in air at 650°C for 5 h. Bead milling was performed with a bead mill (Labstar HFM02, Ashizawa Finetech) and zirconia beads with a diameter of 30 μm or 0.1 mm (Nikkato). A slurry was prepared by mixing 361 g of zirconia beads and 0.464 g of LCO in 130 mL of ethanol. The slurry was milled for 2 h. The zirconia beads were separated using a 635-mesh sieve, and the resulting slurry containing LCO was evaporated to dryness to obtain a powder. For the preparation of catalyst suspensions, the LCO was mixed with carbon (Ketjen Black EC600JD, Lion) at a 3:7 mass ratio of oxide to the carbon in 2-propanol solvent (Wako Pure Chemical) by ultrasonication (40 kHz) for 30 min. Experimental details of the material and electrochemical characterizations are shown in the supporting information. Linear sweep voltammetry (LSV) was conducted in a three-electrode electrochemical cell using RDE, which was prepared by catalyst loading of 0.10 mg cm^{−2}. A reference electrode was an Hg/HgO electrode, a counter electrode was a platinum wire, and the electrolyte was a 1.0 M KOH solution.

Figure 1. XRD patterns of (a) as-synthesized LCO, (b) LBM-LCO, and (c) CBM-LCO.

Table 1. Crystallite size, BET surface area, and mean agglomerate size of as-synthesized LCO, LBM-LCO, and CBM-LCO.

	Crystallite size /nm	BET surface area /m ² g ⁻¹	Mean agglomerate size /nm
As-synthesized LCO	32.6	11.5	698
LBM-LCO	26.0	51.7	77
CBM-LCO	9.5	56.8	94

3. Results and Discussion

XRD patterns of LCO before and after bead milling are shown in Fig. 1. It can be seen that the XRD patterns are identical to the standard values (JCPDS-ICDD Card No. 00-048-0123), which can be readily indexed to the trigonal phase of LCO (space group: $R\bar{3}c$, 167). After milling with 30- μm beads at a rotation speed of 6 m s^{-1} , the XRD pattern of the low-energy bead-milled LCO (LBM-LCO) maintains the perovskite crystalline phase with no other peaks assignable to the formation of secondary phases. As a comparison, an XRD pattern of LCO milled using 0.1 mm beads at a rotation speed of 15 m s^{-1} , corresponding to conventional milling conditions, is included in Fig. 1. The diffraction peaks of the conventional bead-milled LCO (CBM-LCO) assigned to the perovskite structure indicated that the crystallinity of the sample partially persisted; however, the relative crystallinity percentage and crystallite size were significantly decreased to 32% and 9.5 nm, respectively. Although BET surface area and mean agglomerate size of CBM-LCO were much higher and smaller, respectively, than those of as-synthesized LCO (Table 1), the shear stress and the collision force from large beads provided a considerably strong energy that broke the main body of the crystal in the high-energy bead milling process.

LCO was mixed with carbon in 2-propanol by ultrasonication for 30 min. To visually evaluate the degree of the dispersion of LCO nanoparticles on the carbon, the samples were observed by STEM (Fig. 2). Strong dark areas and weak dark areas indicate the presence of LCO and the carbon support, respectively, because the micrographs are bright-field images. Only ultrasonic agitation did not give a good dispersion of LCO nanoparticles. Large agglomerates with size ranging from a few hundred nm to over 1 μm , which consisted

Figure 2. STEM images of (a, d) as-synthesized LCO/carbon, (b, e) LBM-LCO/carbon, and (c, f) CBM-LCO/carbon (images a, b, and c were scaled to the same magnification). Samples were deposited on holey carbon grids.

of loosely bound primary particles, were observed for as-synthesized LCO/carbon. It can be speculated that high temperature calcination, which was required for the phase formation, caused agglomeration of the adjacent particles, resulting in low dispersion of the oxide nanoparticles. However, through bead milling processes, LCO was finely dispersed on carbon. Isolated nanoparticles of approximately 30 nm and small agglomerates of around 100 nm in size of LBM-LCO were observed. These results indicate that the low-energy bead-milling process can break the oxide agglomerates, while suppressing the damage to the crystal structure, resulting in high dispersion of the oxide nanoparticles.

The oxygen reduction activity of LCO/carbon composites was measured by using RDE. LSV curves (Fig. 3 and S1) indicate that the limiting current density increases with increasing rotation rate due to the shortened diffusion layer. In the Koutecky–Levich plots (inset of Fig. 3), nearly identical slopes were observed, suggesting that the oxide dispersion did not affect the overall electron transfer numbers for the oxygen reduction reaction ($n = 3.7$). However, a positive shift of ~ 0.03 V for the half-wave potential measured at 1,600 rpm was observed for LBM-LCO/carbon in comparison with as-synthesized LCO/carbon. The kinetic current density corrected for the mass-transport effects of LBM-LCO/carbon is 2.47 mA cm^{-2} at -0.15 V, which is 2.7 times higher than that of the as-synthesized LCO/carbon (0.91 mA cm^{-2}). In heterogeneous catalysis, the catalytic activity strongly depends on the surface geometric factor. Many reports have suggested that catalyst nanoparticles with large surface area and fine dispersion are beneficial for the oxygen reduction reaction.^{7–9,15,16} The enhancement of the oxygen reduction

Figure 3. LSV curves of as-synthesized LCO/carbon, LBM-LCO/carbon, and CBM-LCO/carbon at a rotation rate of 1,600 rpm in O₂-saturated 1.0 M KOH. The inset shows Koutecky–Levich plots obtained from the LSV curves at -0.25 V.

activity may be attributed to the enlarged surface area and improved dispersion of LCO. According to a theory proposed by Watanabe,⁸ there is a potential reaction space around each active site for the oxygen reduction. The oxygen reduction activity will decrease when overlapping of the space occurs by a decrease in the distance between the active sites.^{8,17} The increase in the degree of dispersion of LCO could avoid this interference between the active sites. A further study is in progress to elucidate the detailed mechanism of the enhancement. In comparison with LBM-LCO/carbon, CBM-LCO/carbon displayed low half-wave potential (-0.17 V) and small kinetic current density (1.11 mA cm⁻²). The B-site transition metal cations in perovskites (ABO₃) are mainly considered as the active sites for oxygen reduction catalysis.^{1,18,19} Bead milling under conventional conditions (bead size: 0.1 mm, rotation speed: 15 m s⁻¹) dispersed the agglomerated LCO nanoparticles but caused the serious destruction of the crystal structure, which may result in a decrease in the number of active B (Co) sites in the perovskite.

4. Conclusion

LCO/carbon catalyst was prepared via bead milling using small beads at a low rotation rate. The small beads have a low energy and

minimize damage to the crystal structure of the oxide. LBM-LCO was dispersed on carbon in the form of isolated nanoparticles of ~ 30 nm in size and small nanoparticle agglomerates of ~ 100 nm. Likely due to the large surface area and fine dispersion of the oxide, the LBM-LCO/carbon displayed improved activity in the electrochemical reduction of oxygen when compared with that displayed by the as-synthesized LCO/carbon.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.18-00094>.

References

1. Y. Zhu, W. Zhou, and Z. Shao, *Small*, **13**, 1603793 (2017).
2. T. Hyodo, M. Hayashi, N. Miura, and N. Yamazoe, *J. Electrochem. Soc.*, **143**, L266 (1996).
3. D. Chen, C. Chen, Z. M. Baiyee, Z. Shao, and F. Ciucci, *Chem. Rev.*, **115**, 9869 (2015).
4. J. Jung, M. Risch, S. Park, M. G. Kim, G. Nam, H. Jeong, Y. Shao-horn, and J. Cho, *Energy Environ. Sci.*, **9**, 176 (2016).
5. D. Meadowcroft, *Nature*, **226**, 847 (1970).
6. Y. Teraoka, H. Kakebayashi, I. Moriguchi, and S. Kagawa, *Chem. Lett.*, **20**, 673 (1991).
7. M. Yuasa, K. Shimanoe, Y. Teraoka, and N. Yamazoe, *Electrochem. Solid-State Lett.*, **14**, A67 (2011).
8. M. Watanabe, H. Sei, and P. Stonehart, *J. Electroanal. Chem.*, **261**, 375 (1989).
9. M. Yuasa, N. Tachibana, and K. Shimanoe, *Chem. Mater.*, **25**, 3072 (2013).
10. R. R. Retamal Marin, F. Babick, and M. Stintz, *Powder Technol.*, **318**, 451 (2017).
11. T. Ogi, R. Zulhijah, T. Iwaki, and K. Okuyama, *KONA Powder Part. J.*, **34**, 3 (2017).
12. Y. Yamamoto, M. Kawayara, H. Segawa, S. Uchida, J. Kano, F. Saito, K. Tsujimoto, T. Saito, and S. Ito, *Chem. Lett.*, **40**, 1220 (2011).
13. C. Schilde, C. Mages-sauter, A. Kwade, and H. P. Schuchmann, *Powder Technol.*, **207**, 353 (2011).
14. M. Matsuoka, J. Tatami, T. Wakihara, K. Komeya, and T. Meguro, *J. Asian Ceram. Soc.*, **2**, 199 (2014).
15. Y. Wei, C. Liu, and K. Wang, *ChemPhysChem*, **11**, 3078 (2010).
16. J. Tulloch and S. W. Donne, *J. Power Sources*, **188**, 359 (2009).
17. J. Maruyama, T. Hasegawa, S. Iwasaki, H. Kanda, and H. Kishimoto, *ACS Sustain. Chem. Eng.*, **2**, 493 (2014).
18. J. Suntivich, H. A. Gasteiger, N. Yabuuchi, H. Nakanishi, J. B. Goodenough, and Y. Shao-Horn, *Nat. Chem.*, **3**, 546 (2011).
19. Y. Matsumoto, H. Yoneyama, and H. Tamura, *J. Electroanal. Chem.*, **83**, 237 (1977).