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알칼리용액에서 $La_{0.8}Sr_{0.2}MnO_3$ 페롭스카이트 촉매의 산소환원 및 발생반응에서 도전재의 영향

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Effect of Conductive Additives in $La_{0.8}Sr_{0.2}MnO_3$ Perovskite Electrodes for Oxygen Reduction and Evolution in Alkaline Solution

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Abstract >> The effects of conductive additives in a $La_{0.8}Sr_{0.2}MnO_3$ perovskite bifunctional electrode for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) were investigated in an alkaline solution. Highly porous carbon black (CB) and Ni powder were added to the bifunctional electrodes as conductive additives. The surface morphologies of electrodes containing CB and Ni were observed by scanning electron microscopy (SEM). The current densities for both ORR and OER were changed by the addition of CB. The conductive additive changed physical properties of bifunctional electrodes such as the sheet conductance, gas permeability and contact angle. It was observed that the air permeability of electrode was most effective to enhance the currents for ORR and OER.

Key words : Perovskite (페롭스카이트), $La_{0.8}Sr_{0.2}MnO_3$, electrode (전극), conductive additive (도전재), oxygen reduction (산소환원), oxygen evolution (산소발생)

1. Introduction

Although Zn-air rechargeable batteries (ZARB) have received substantial attention because of their low cost, high stability, non-explosiveness, and environmental friendliness, no attractive advantages of these batteries have been recorded because of their poor cycleability, the high solubility of zinc compounds, and low rates of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) of air electrodes[1,2]. Platinum is well known as the best ORR catalyst in fuel cells, but it has only moderate activity for the OER[3]. The catalytic activities of perovskite-type materials, such as La-based oxides, as non-precious materials and related compounds have also received much attention because of their

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relatively high catalytic activity for the ORR and OER and their low-cost syntheses[4,5] relatively compared to Pt catalyst.

Gas diffusion electrodes (GDEs) typically consist of a catalyst, a conductive additives, and a polymer binder. Carbon materials have been widely used as conductive additives to increase electric conductivity of the porous electrodes. The carbon content and morphology in GDEs play a critical role in cell performance because that it affects to the pore structure and electric conduction. Nishio et al. reported that the carbon content and surface area in the electrode affected current densities and durabilities[6]. Additionally, the presence of carbon in perovskite composite electrodes was observed to promote the reduction of O_2 to H_2O_2 via two electron reaction in the ORR, followed by perovskite -catalyzed reduction and/or decomposition of H_2O_2[7]. However, the corrosion of carbon in alkaline solution has been reported to occur, leading the formation of CO, CO_2, surface oxides, and organic-carbon products[8]. Staud and Ross observed that the corrosion of acetylene black (a type of carbon black (CB)) was accelerated by catalyzing with metal oxides (cobalt oxide, nickel oxide, and iron oxide)[9].

Ni powder, highly conductive and chemically stable in alkaline media, was investigated as conductive filler for GDEs. Shim and Lee reported that the oxidation of hydrogen in a Raney Ni electrode in alkaline solution was improved by the addition of Ni powder[10]. When Ni was immersed in alkaline solution, the surface was covered by a hydroxide film ($Ni(OH)_2$). When the potential was increased to 0.4 V (vs. Hg/HgO), the hydroxide phase was oxidized to form nickel oxyhydroxide (NiOOH)[11].

In this study, the electrochemical properties of La-based perovskite bifunctional electrodes were characterized by varying the conductive additives for ORR and OER in alkaline solution. CB and Ni powder were selected as conductive additives. Changes in the electrochemical performance and physical properties were analyzed according to the conductive additive contents.

2. Experimental

The catalytic layers of the bifunctional electrodes were prepared according to the following process: $La_{0.8}Sr_{0.2}MnO_3$ (L8S2MO) (Fuel cell materials) powders were mixed with carbon black (CB) (Vulcan XC-72, Cabot) or fine Ni (255, Vale) powders in a mixture of water/ethanol. The mixture solution was ultrasonically treated for 5 min, and then, polytetrafluoroethylene (PTFE, 60% dispersion, DuPont) was added. The mass ratio of PTFE was 10% of the total mass. The detail composition of electrodes is listed in Table 1. The

Table 1 Electrode compositions and their physical and electrochemical properties

L8S2MO	CB	Ni	PTFE	I(mA/cm^2) at 0.8V	I(mA/cm^2) at 2.4V	Air permeability (x10^{-12}m^2)	Sheet Conductance (x10^{-3}S·£)	Contact angle (°)
20	5	65	10	59.4	74.7	14.1	2.79	137.4
20	10	60	10	102.0	124.5	17.4	7.25	143.0
20	20	50	10	74.5	79.4	13.4	16.09	150.0
20	35	35	10	51.2	55.2	16.0	31.52	153.9
20	50	20	10	54.6	33.8	18.0	37.74	151.3
20	70	0	10	32.7	22.9	10.6	36.83	143.6

solution was dried at 60°C to obtain the mixture powders. The mixture was kneaded and rolled by two metal rollers with the addition of a small amount of isopropyl alcohol to produce a sheet-type catalytic layer. The gas diffusion layers (GDLs) were prepared by following same procedure used for the catalyst layer. The CB powder was mixed with the Ni powder and PTFE. The mass ratio of PTFE was 40% of the total mass. The bifunctional electrodes were prepared by hot pressing the catalyst layer with the GDL and Ni mesh (Dexmet) as the current collector at 350°C for 5 min.

The bifunctional electrodes were electrochemically characterized for the ORR and OER in 8 M KOH solution using a three-electrode system. The working electrode was 1 cm^2 in size and cut into a round shape. The counter and reference electrodes consisted of a Pt mesh and a Zn wire with a diameter of 1 mm, respectively. The electrochemical experimentals were conducted at room temperature. In the three-electrode systems, the catalytic layer made contact with the KOH solution, and the GDL was exposed to the air atmosphere without the forced air-feeding. The cell potential and current was measured using a linear sweep voltammetry (LSV) method at a scan rate of 1 mV/s[12)]. The scanning was conducted for 20 times between 0.8 and 2.5 V vs. Zn/Zn^{2+}, which corresponded to -0.413 and 1.287 V vs. SHE (standard hydrogen electrode), and results were collected at final cycle.

The surface morphology of the catalytic layer was observed by field emission- scanning electron microscopy (FE-SEM, Hitachi, S-4800). The sheet resistance (in-plane) of the electrodes without GDLs was measured using the four-point probe method with a conductivity meter (Changmin Tech, CMT-SR-100N). To compare the air flux through a plane (along the z direction) of the electrodes, their air permeabilities were measured with a lab-made instrument using modified Gurley method. This instrument, a permeometer, measured the air flow per minute at water pressure drop of 1.27 cm (0.5 inch) between the gas inlet and outlet. The air permeability was calculated according to Darcy' law[13-15)]. Those properties of electrodes were analyzed before electrochemical experiment.

3. Results and discussion

Fig. 1 shows SEM images of L8S2MO electrodes containing various amounts of CB with Ni powder, respectively. The electrode with 5% CB contained most of L8S2MO particles on its surface, and the amount of CB on the surface increased as its content increased.

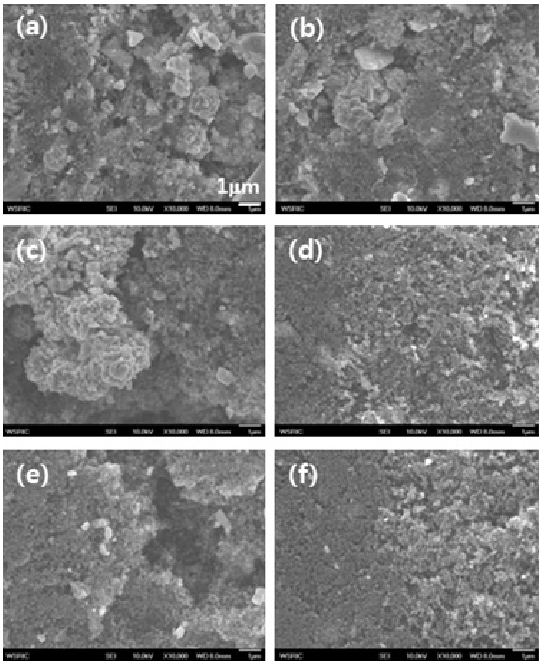

Fig. 1 SEM images of carbon black containing electrodes. Carbon black content (a) 5%, (b) 10%, (c) 20%, (d) 35%, (e) 50%, (f) 70%

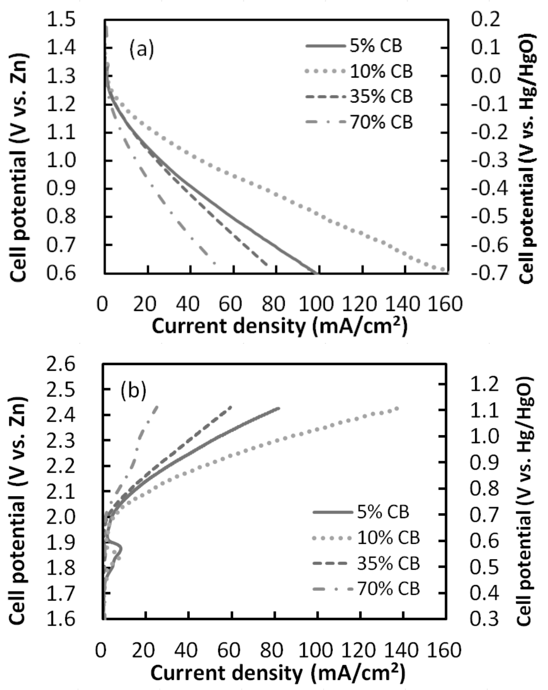

Fig. 2 Linear sweep voltammograms of L8S2MO electrodes with different carbon black content for (a) ORR and (b) OER in an 8M KOH solution

We assumed that L8S2MO perovskite was favorable for the ORR and that Ni powder was favorable for the OER because the former has been known as a good catalyst relative to Pt and because the latter has good electric conductivity. Fig. 2 shows LSVs of L8S2MO electrodes with different CB contents for the ORR and OER in 8 M KOH solution. These electrodes contained 20% L8S2MO and 10% PTFE with the remainder consisting of CB and Ni. For the ORR, the electrode containing 10% CB (60% Ni) exhibited the best performance, and that without CB (70% Ni) showed the lowest performance. The electrode with 10% CB also showed the highest performance for the OER, but that containing 70% CB (0% Ni) exhibited the lowest performance for the OER. Unlike the results of the ORR test, the electrode without CB (70% Ni) exhibited higher performance than those with 35 and 70% CB for the OER. The electrodes without CB and without Ni showed the lowest performance for the ORR and OER, respectively. The highest performance for both the ORR and OER was exhibited by the electrode containing 10% CB (60% Ni).

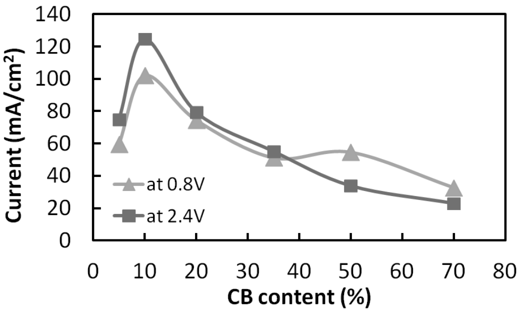

Fig. 3 Current as a function of CB content at 0.8 and 2.4 V for ORR and OER

Fig. 3 shows the currents of electrodes with different Ni and CB contents at 0.8 and 2.4V for the ORR and OER, respectively. Also, the current values, which were average valuescalculated from three tests, are listed in Table 1. The current was the highest at 10% and 60% Ni contents for the ORR and OER, respectively. However, the electrode containing 10% CB showed the highest current for both the ORR and OER. When the CB content exceeded 10%, the current continuously decreased.

The electrodes' sheet resistances as manufactured were measured using 4-probe conductivity meter and are shown in Fig. 4 (a). These resistances correspond to the apparent sheet resistances of the catalytic layer only. The resistances sharply decreased as the CB content increased. The small particle size and dispersion of CB in the electrode influenced the electrode's conductivity[16,17]. It means that the Ni powder consisted of large particles, relative to those of CB, and despite the high conductivity of the Ni material itself, smaller particles were more effective to sheet resistance than larger particle.

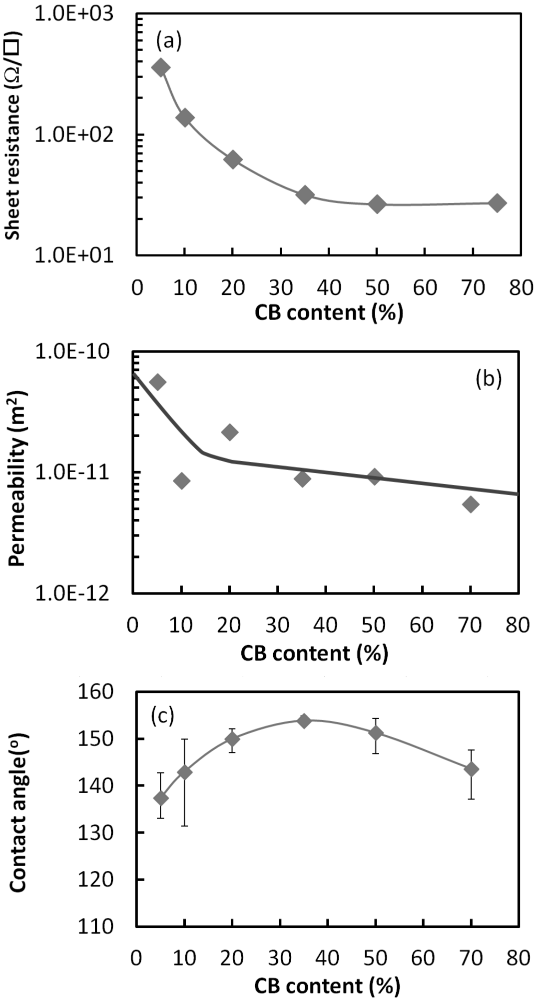

Fig. 4 (a) Sheet resistance (in-plane), (b) air permeability constants and (c) contact angles of electrodes as a function of CB content

As shown in Fig. 4 (b), the air permeability of the electrodes containing CB decreased as their contents increased. For electrodes with CB, because the particle size of CB is smaller than that of L8S2MO, the pore area is likely to increase and the pore channels become narrow as the CB content increases; however, the pore size distributions of the electrodes were not analyzed using analytical instruments, such as a mercury porosimeter[18]. The SEM images in Fig. 1 confirmed that larger particles disappeared as the CB content increased. The surface area of the Ni powder was ~0.7 m^2/g (supplied by the manufacturer), which was much lower than that of L8S2MO (13~18 m^2/g; supplied from manufacturer). Fig. 4 (c) shows the contact angle of the electrodes' surfaces according to their CB contents. The maximum values were observed at 35% CB and 60% Ni powder. The contact angle of binder, PTFE, is *ca.* 150^o, which is highly hydrophobic Fig. 4. (a) Sheet resistance (in-plane), (b) air permeability constants and (c) contact angles of electrodes as a function of CB content material[19]. Gostick et al. reported that a carbon layer containing PTFE on carbon paper, known as a micro-porous layer (MPL) in the field of fuel cell application, showed a contact angle of *ca.* 153^o [20]. When the ratio of CB content was low, the hydrophilic perovskite oxide occupied a large portion in the surface of electrode, and the contact angle was low. However, when the ratio of CB content was increased, the volumetric ratio of PTFE decreased relative to that of the bulky CB[21]. Thus, the contact angle decreased further.

The relationships between the physical properties of the electrodes and the current for the ORR and OER are summarized in Fig. 5. As shown in Table 1 and Fig. 4, the physical properties of electrodes were changed with the content of CB. As the current for the ORR and OER increased, the air permeabilities increased slightly, but the sheet conductances decreased sharply, and the contact angles were not changed. The increased air permeability could reasonably increase the current by improving the gas diffusion. However, it is difficult to understand how decreasing the sheet conductance would increase the current. It could be assumed that the conductivity of the electrode does

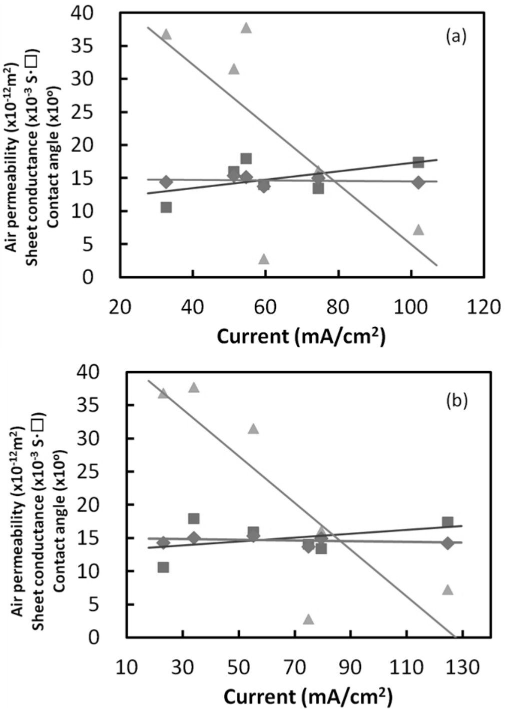

Fig. 5 Air permeability (■), sheet conductance (▲) and contact angle (◆) of electrodes containing CB as a function of current at (a) 0.8 and (b) 2.4V for ORR and OER, respectively

not affect the current of highly conductive electrodes. In this type of the electrode, the gas diffusion through the electrode may be more important than the conductivity[22,23]. 140~150^o of contact angle is enough to keep away flooding of pore and enhance gas diffusion in electrode[20,24,25].

4. Conclusions

The effects of conductive additives (carbon black and Ni powder) in $La_{0.8}Sr_{0.2}MnO_3$ perovskite bifunctional electrodes for the ORR and OER were investigated in alkaline solution. SEM images of the electrodes revealed that the perovskite particles became covered by conductive additives as the additive content increased. The current densities for both the ORR and OER were changed by the addition of CB and Ni. The electrodes containing 10% CB or 60% Ni showed maximum currents for the ORR and OER, respectively. Most of the electrodes' physical properties, the sheet conductance, air permeability, and contact angle, varied as the content of conductive additives varied. It was observed that the air permeability of electrode was most effective property to enhance the currents for ORR and OER.

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References

1. K.A. Striebel, F.R. McLarnon, E.J. Cairns EJ : “Laboratory-scale evaluation of secondary alkaline zinc batteries for electric vehicles”, J. Power Sources, Vol. 47, 1994, p. 1.
2. J.W. Evans, G. Savaskan : “A zinc-air cell employing a packed bed anode”, J. Appl. Electrochem., Vol. 21, 1991, p. 105.
3. Z. Chen, J.Y. Choi, H. Wang, H. Li, Z. Chen : “Highly durable and active non-precious air cathode catalyst for zinc air battery”, J. Power Sources, Vol. 196, 2011, p. 3673.
4. J. Suntivich, H.A. Gasteiger, N. Yabuuchi, H. Nakanishi, J.B. Goodenough, Y. Shao-Horn : “Design principles for oxygen-reduction activity on perovskite oxide catalysts for fuel cells and metal-air batteries”, Nature Chem., Vol. 3, 2011, p. 546.
5. V. Neburchilov, H. Wang, J.J. Martin, W. Qu : “A review on air cathodes for zinc-air fuel cells”, J. Power Sources, Vol. 195, 2010, p. 1271.
6. K. Nishio, S. Molla, T. Okugaki, S. Nakanishi, I. Nitta, Y. Kotani : “Oxygen reduction and evolution reactions of air electrodes using a perovskite oxide

as an electrocatalyst", J. Power Sources, Vol. 278, 2015, p. 645.

7. T. Poux, F.S. Napolskiy, T. Dintzer, G. Kerangueven, S.Y. Istomin, G.A. Tsirlina, E.V. Antipov, E.R. Savinova : "Dual role of carbon in the catalytic layers of perovskite/carbon composites for the electrocatalytic oxygen reduction reaction", Catalysis Today, Vol. 189, 2012, p. 83.
8. K. Kinoshita : "Carbon - Electrochemical and physicochemical properties", John Wiley & Sons, p334, 1988.
9. N. Staud, P.N. Ross : "The Corrosion of Carbon Black Anodes in Alkaline Electrolyte: II. Acetylene Black and the Effect of Oxygen Evolution Catalysts on Corrosion", J. Electrochem. Soc., Vol. 133, 1986, p. 1079.
10. J. Shim, H.K. Lee : "Improved performance of Raney nickel electrode by the addition of electrically conductive materials for hydrogen oxidation reaction", Mater. Chem. Phys., Vol. 69, 2001, p. 72.
11. S.L. Medway, C.A. Lucas, A. Kowal, R.J. Nichols, D. Johnson : "In situ studies of the oxidation of nickel electrodes in alkaline solution", J. Electroanal. Chem., Vol. 587, 2006, p. 172.
12. K. Lopez, G. Park, H.J. Sun, J.C. An, S. Eom, J. Shim : "Electrochemical characterizations of $LaMO_3$ (M = Co, Mn, Fe, and Ni) and partially substituted $LaNi_xM_{1-x}O_3$ (x = 0.25 or 0.5) for oxygen reduction and evolution in alkaline solution", J. Appl. Electrochem., Vol. 45, 2015, p. 313.
13. F.A.L. Dullien : "Porous Media: Fluid Transport and Pore Structure", Academic Press, New York, 1992.
14. J. Geertsma : "Estimating the coefficient of inertial resistance in fluid flow through porous media", Soc. Pet. Eng. J., Vol. 10, 1974, p. 445.
15. J. Shim, C. Han, H.J. Sun, G. Park : "Preparation and Characterization for Carbon Composite Gas Diffusion Layer on Polymer Electrolyte Membrane Fuel Cells", Trans. Kor. Hydrogen New Energy Soc., Vol. 23, 2012, p. 34.
16. K. Miyasaka, K. Watanabe, E. Jojima, H. Aida, M. Sumita, K. Ishikawa : "Electrical conductivity of carbon-polymer composites as a function of carbon content", J. Mater. Sci., Vol. 17, 1982, p. 1610.
17. O. Meincke, D. Kaempfer, H. Weickmann, C. Friedrich, M. Vathauer, H. Warth : "Mechanical properties and electrical conductivity of carbon-nanotube filled polyamide-6 and its blends with acrylonitrile/butadiene/styrene", Polymer, Vol. 45, 2004, p. 739.
18. C. Han, I.T. Kim, H.J. Sun, G. Park, J.J. Lee, H.K. Lee, J. Shim : "Effect of Carbon Content on the Physical Properties of Carbon Composite Gas Diffusion Layer in PEMFCs", Int. J. Electrochem. Sci., Vol. 7, 2012, p. 8627.
19. A.W. Adamson : "Physical Chemistry of Surfaces", John Wiley and Sons, New York (1982).
20. J.T. Gostick, M.W. Fowler, M.A. Ioannidis, M.D. Pritzker, Y.M. Volfkovich, A. Sakars : "Capillary pressure and hydrophilic porosity in gas diffusion layers for polymer electrolyte fuel cells", J. Power Sources, Vol. 156, 2006, p. 375.
21. T. Hang, A. Hu, H. Ling, M. Li, D. Mao : "Super-hydrophobic nickel films with micro-nano hierarchical structure prepared by electrodeposition", Appl. Surf. Sci., Vol. 256, 2010, p. 2400.
22. J. Shim, Y.S. Park, H.K. Lee, J.S. Lee : "Hydrogen oxidation characteristics of Raney nickel electrodes with carbon black in an alkaline fuel cell", J. Power Sources, Vol. 74, 1998, p. 151.
23. J. Kim, Y. Lee : "Preparation of Electrode Using Ni-PTFE Composite Plating for Alkaline Fuel Cell", Trans. Kor. Hydrogen New Energy Soc., Vol. 20, 2009, p. 361.
24. F. Bidault, D.J.L Brett, P.H. Middleton, N.P. Brandon : "Review of gas diffusion cathodes for alkaline fuel cells", J. Power Sources, Vol. 187, 2009, p. 39.
25. M. Jeong, K. Song, T. Cho, W. Choi : "Water Repellent Coating of GDL with Different Concentration of Nano-sized PTFE Solution", Trans. Kor. Hydrogen New Energy Soc., Vol. 20, 2009, p. 323.