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Electrochemical Properties of Low Bi Doped $La_{0.60}Dy_{0.10}Sr_{0.30}Mn_{(1-x)}Bi_xO_3$ Perovskite Materials

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Abstract

Developing low-cost, high-durability and high-performance electrocatalytic materials are needed for hydrogen/oxygen evolution (HER/OER) and oxygen reduction reactions (ORR) which are crucial steps for regenerative fuel cells. Although Pt-based, RuO_2 and IrO_2 materials are widely used for these purposes, other alternative materials are required with desired properties. In this regard, we studied the electrochemical properties of lanthanum-based perovskites which were synthesized by sol-gel method. We investigated the substitution of 10% Dy and 30% Sr into the A site and a small amount of Bi (x: 0, 0.03 and 0.1) added into the B site of $La_{0.60}Dy_{0.10}Sr_{0.30}Mn_{(1-x)}Bi_xO_3$ perovskites on HER, OER and ORR in 1 M KOH alkaline media at room temperature. While undoped and 3% Bi doped samples exhibited poor HER activities, the effect of 10% Bi in the structure enhanced HER activities by lowering onset potential from -1.389 V to -1.036 V (vs. Ag/AgCl) and increasing specific current density from -13.3 mA cm^{-2} to -121.8 mA cm^{-2} at -1.4 V. Similarly, OER activity was also improved due to 10% Bi and onset potential and specific current density was found to be 0.758 V and 88.3 mA cm^{-2}, respectively. The large Tafel slopes indicate that the ORR mechanism is possible in the structure but at a slow rate. The addition of 10% Bi in the structure resulted in a very high resistance of 19.3 kΩ and it reduced to a desired value of 3.5 kΩ due to ion conducting paths developed in the catalysts.

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***Keywords**:* La-based perovskite; Low Bi-doping; Electrochemistry; HER; OER; ORR.

Düşük Bi Katkılı Manyetikalorik $La_{0.60}Dy_{0.10}Sr_{0.30}Mn_{(1-x)}Bi_xO_3$ Perovskite Malzemelerin Elektrokimyasal Özellikleri

Öz

Rejeneratif yakıt hücreleri için çok önemli adımları olan hidrojen/oksijen evrimi (HER/OER) ve oksijen indirgeme reaksiyonlarının (ORR) düşük maliyetli, yüksek dayanıklılığa sahip ve yüksek performanslı elektrokatalitik malzemelerin geliştirilmesine ihtiyaç duyulmaktadır. Pt esaslı, RuO_2 ve IrO_2 malzemeler bu amaç için yaygın olarak kullanılsa da, istenilen özelliklerde alternatif malzemelere ihtiyaç duyulmaktadır. Bu bağlamda sol-jel yöntemi ile sentezlenen lantan bazlı perovskitlerin elektrokimyasal özelliklerini çalıştık. $La_{0.60}Dy_{0.10}Sr_{0.30}Mn_{(1-x)}Bi_xO_3$ perovskit yapısında, A bölgesine %10 Dy ve %30 Sr ve B bölgesine az miktarda Bi (x: 0, 0.03 ve 0.1) katkılanmasını oda sıcaklığında 1 M KOH alkali ortamda HER, OER ve ORR araştırdık. Katkılanmamış ve %3 Bi katkılanmış örnekler zayıf HER aktiviteleri sergilerken, yapıdaki %10 Bi'nin etkisi başlangıç potansiyelini -1,389 V'tan -1,036 V'a düşürerek (Ag/AgCl'ye karşı) ve spesifik akımı yoğunluğunu -13,3 mA cm^{-2}'den -121,8 mA cm^{-2}'ye -1,4 V'ta arttışını sağladı. Benzer şekilde OER aktivitesi de %10 Bi sayesinde iyileşmiş ve başlangıç potansiyeli ve özgül akım yoğunluğu sırasıyla 0,758 V ve 88,3 mA cm^{-2} olarak bulunmuştur. Büyük Tafel eğimleri, ORR mekanizmasının yapıda gerçekleşebildiğini ancak yavaş bir hızda olduğunu göstermektedir. Yapıya %10 Bi ilavesi 19,3 kΩ gibi çok yüksek bir direnç ile sonuçlanmış ve katalizörlerde oluşan iyon iletim yollarından dolayı 3,5 kΩ gibi istenen bir değere düşmüştür.

Anahtar Kelimeler: La bazlı perovskit; Düşük Bi-katkılama; Elektrokimya; HER; OER; ORR.

1. Introduction

Since the general structure of perovskites is identified as ABO_3 which has received significant attention in chemistry and physics and all $ABO_{3\pm\delta}$ structures similar to this structure are called perovskites [1, 2]. Here, A is a cation in the structure and has a larger ionic radius that makes 12 bonds with oxygen. On the other hand, the atom in the B position has a smaller radius and makes 6 bonds with oxygen. While A atom and oxygens form a cubic structure, B is located in the octahedral spaces in this closed cubic structure. For A and B elements to form the perovskite structure, the tolerance factor (*t*) must be between 0.75 and 1. The tolerance factor is calculated based on the radius of the ions of atoms [3]. The tolerance factor of many perovskite structures

studied in the literature ranges from 0.8 to 0.9. For the formation of perovskite structure, r_A>0.090 nm and r_B must be >0.051 nm [4]. The number of electrons of A and B ions in the structure must be balanced with oxygen which can be given with $A^{+1}B^{+5}O_3$, $A^{+2}B^{+4}O_3$ or $A^{+3}B^{+3}O_3$. With the second A and B elements added to the structure, the perovskite structure lose its ideal structure. In this case, orthorhombic, rhombohedral, tetragonal, monoclinic and triclinic structures can be formed.

Perovskites usually provide different physical properties, such as ferroelectric ($BaTiO_3$) ferromagnetic ($SrRuO_3$) superconductivity and thermal conductivity ($LaCoO_3$) behaviors which allows in many application areas in magnetic and electronic magnetocaloric effect [3, 5-8]. La-based materials were widely investigated to determine magnetocaloric properties and also studied doping these perovskites of A or B sites with Sr, Dy, Bi, Ba, K, Cu, Co, Ru, etc. [9-11]. For example, $La_{0.7}Sr_{0.3}MnO_3$ compound, which was synthesized by solid-state reaction method, increased the value of the magnetic entropy from 4.56 J/kg K for the undoped sample to 5.02 J/kg K with the substitution of Bi, but further increase the Bi ratio decreased the magnetic entropy [12]. Similarly, Dhahri et al. [13] studied the structural, magnetic and magnetocaloric properties of $La_{0.67-x}Bi_xBa_{0.33}MnO_3$ compound, which was synthesized by sol-gel method. They reported that all compounds exhibited a second-order magnetic phase transition and the transition temperature decreased with increasing Bi doping ratio.

Typically, noble metals (usually Pt, Pd-based) catalysts utilize for hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) while they exhibit rather poor activity for oxygen evolution reaction (OER) [14]. Besides, RuO_2 and IrO_2 have been also used for OER and ORR reactions [15]. However, efficient, low-cost, high-durability catalysts were required for mass production. One possible candidate for these purposes takes into account perovskite materials for OER and ORR processes with high-temperature durability and high conductivity [16]. For instance, bifunctional $La_{1-x}Sr_xFeO_{3-\delta}$ based perovskite has been used for cathodic and anodic material in high-temperature fuel cells and electrolyzes, respectively [17]. Here, reducing La and increasing Sr in the A site increases the oxygen vacancies which plays a crucial role for OER and also controlling the B site composition ratio in the structure enhances ORR.

Although the structural and magnetocaloric properties of $LaXMnO_3$-based perovskites have been widely investigated for different purposes, there is no detailed study of the catalytic properties of these perovskites. In this paper, we aimed to provide first principle investigations on the electrocatalytic properties of cost-effective $La_{0.60}Dy_{0.10}Sr_{0.30}Mn_{(1-x)}Bi_xO_3$ perovskites which are synthesized by sol-gel method. The electrocatalytic performance of $La_{0.60}Dy_{0.10}Sr_{0.30}Mn_{(1-}$

$_{x)}Bi_xO_3$ perovskites catalysts will be reported for HER, ORR and OER via cyclic voltammetry, linear sweep voltammetry, Tafel slope and impedance measurements.

2. Materials and Methods

2.1. Synthesis of Bi doped LDSM magnanites

$La_{0.60}Dy_{0.10}Sr_{0.30}Mn_{(1-x)}Bi_xO_3$ (x=0, 0.03 and 0.1) manganites with abbreviations as LDSM, LDSM+3% Bi and LDSM+10% Bi for x=0, 0.03 and 0.1, respectively, were produced by sol-gel method. Firstly, the appropriate amounts of the starting compounds were weighed and their aqueous solutions were prepared. These prepared solutions were mixed in a heated magnetic stirrer at 300. Appropriate agents, citric acid and ethylene glycol, were added to the mixture in appropriate amounts for the solution to gel. Then, the resulting mixture was heat treated at 550 for 1 h in order to be properly removed from the beaker. The material extracted from the beaker in powder form was then calcined 600 for 6 hours to remove the organic compounds from the structure. After the grinding and pressing processes, the material was sintered at 1200 for 24 h in air atmosphere.

2.2. Electrocatalysts preparation

The electrochemical measurements were performed using Gamry 1010E potentiostat/galvanostat three-electrode system in which carbon rode (5 mm dia, 0.1963 cm^2 area), platinum foil (66 mm^2) and Ag/AgCl in 3 M KCl solution were used as working, counter and references electrodes. We mixed 10 mg LDSM catalysts with 25 µl ethylene glycol (extra pure), 15 µl isopropanol and 5 µl 5% Nafion and sonicated for 30 min and then vortexed for 3 min. We loaded 1 mg catalysts ink on the working electrode and dried up the electrodes in a furnace at 55°C for 16 h prior to electrocatalytic performance.

3. Results

In order to investigate the electrocatalytic properties of Bi-doped $La_{0.60}Dy_{0.10}Sr_{0.30}Mn_{(1-x)}Bi_xO_3$ manganites, we first performed CV measurements. As seen in Figure 1, CV curves of LDSM (black), LDSM+3% Bi (red) and LDSM+10% Bi (blue) perovskites were recorded between -1 V and 1 V (vs. Ag/AgCl) with a scan rate of 50 mV s^{-1} in 1 M KOH alkaline media at room temperature. We can clearly distinguish the regions for HER, OER and ORR for all samples. Although, the substitution of 3% Bi (red) in LDSM structure did not affect the hydrogen gas evolution in the cathodic reduction region, increasing this ratio to 10% Bi (blue) enhanced HER activity with a clearly increased current density and lowered onset potential. In this region, we also observed modified ORR activity as a function of Bi substitution. Both the current density

and onset potential were improved by increasing the Bi ratio to 10% in the structure. On the other hand, the substitution of both 3% and 10% Bi samples provided better oxygen gas evolution in the anodic region in comparison with undoped-LDSM sample. These results indicate that 10% Bi-doped LDSM materials promise good electrocatalytic performance for HER and OER activities.

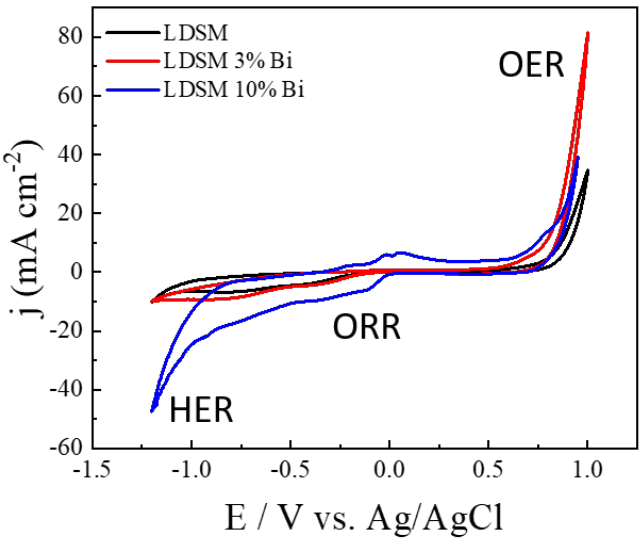

Figure 1: Cyclic voltammogram curves of LDSM (black), LDSM+3% Bi (red) and LDSM+10% Bi (blue) perovskites recorded between -1 V and 1 V (vs. Ag/AgCl) with a scan rate of 50 mV s^{-1} in 1 M KOH alkaline media at room temperature

We further performed a detailed investigation of current densities as a function of applied voltage for HER, ORR and OER activities for $La_{0.60}Dy_{0.10}Sr_{0.30}Mn_{(1-x)}Bi_xO_3$ manganites in 1 M KOH alkaline media at room temperature (see Figure 2(a-b)). The HER and OER performance of the manganites were illustrated in Figure 2(a) and the onset potential and specific current density were reported in Table 1. However, LDSM and LDSM+3% Bi catalysts exhibited highly poor HER activities of -1.389 V and -1.352 V, respectively. It can be clearly seen that the substitution of 10% Bi vastly improved HER performance with an onset potential of -1.036 V (vs. Ag/AgCl) and this value is close to HER activity of the commercially available Pt/C (20.7 mV vs. RHE) [18]. Moreover, the performance of ORR activity for LDSM and LDSM+3% Bi catalysts is highly low and required high activation voltage over -0.15 V. However, 10% Bi substitution lowered the potential by about 90 mV. The onset potential of LDSM, LDSM+3% Bi and LDSM+10% Bi were found to be 0.853 V, 0.769 V and 0.758 V, respectively. Here, 10% Bi substitution also improved the activity by about 100 mV. Similarly, the largest specific current density is measured as 88.3 mA cm^{-2} at 1 V for the substitution of the 10% Bi in LDSM structure. A similar result was reported in the literature as 80 mA cm^{-2} for $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$/carbon composite [19].

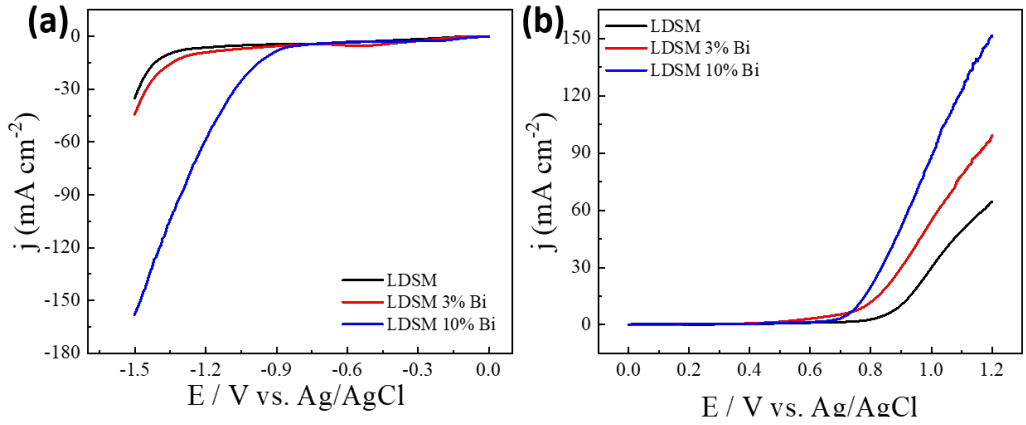

Figure 2: Current densities of LDSM (black), LDSM+3% Bi (red) and LDSM+10% Bi (blue) perovskites for (a) HER activity between 0 V and -1.5 V (vs. Ag/AgCl) and (a) OER activity between 0 V and 1.2 V (vs. Ag/AgCl) with a scan rate of 50 mV s^{-1} in 1 M KOH alkaline media at room temperature

Table 1: The summary of the electrochemical performance of LDSM, LDSM+3% Bi and LDSM+10% Bi manganite given with onset potential and specific current density at -1.4 and 1 V (vs. Ag/AgCl) for HER and OER, respectively

Sample	Onset Potential for HER (V)	Specific *j* for HER at -1.4 V (mA cm^{-2})	Onset Potential for OER (V)	Specific *j* for OER at 1 V (mA cm^{-2})
LDSM	-1.389	-13.3	0.853	29.8
LDSM+3% Bi	-1.352	-20.8	0.769	54.3
LDSM+10% Bi	-1.036	-121.8	0.758	88.3

The electrocatalytic performance of the as-synthesized catalysts as a function of Bi dope was also studied taking into account the Tafel slope (see Figure 3(a)). As seen in Table 2, corrosion potential is negative for 3% and 10% Bi-doped catalysts and this value became positive for undoped LDSM catalysts. We also considered the Tafel slope in cathodic region between -0.1 V and -0.3 V. The large Tafel slope indicates that the ORR mechanism is possible in the structure but at a slow rate. EIS data were also collected between 100 kHz and 0.01 Hz using AC signals of amplitude 10 mV peak to peak at open circuit potential in 1 M KOH solution and fitted with double layer capacitance method for LDSM (black), LDSM+3% Bi (red) and LDSM+10% Bi (blue) perovskites for which typical Nyquist plot is presented in Figure 3(b). The oxygen ion transfer and the surface kinetics occur at high frequency from LDSM sample to the electrolyte and at intermediate frequency, respectively. Here, a small alkali solution resistance, R_{sol}, was recorded between 5.1 Ω and 4.1 Ω [20]. The pore resistance, R_{po} which is ion-conducting paths developed in the catalysts, is reduced from very high resistance 19.3 kΩ to a desired value of 3.5 kΩ due to the substitution of 10% Bi in the structure. The increased C_c value indicates double-layer capacitance which is followed by charge-transfer reaction [21, 22].The effect of Bi doping resulted in oxygen vacancy so that increased adsorbed oxygen species in the structure. Similarly,

hydrogen evolution reaction is enhanced by Bi doping because water molecules are adsorbed by Bi sites. This can be related with reduced pore resistance in 10% Bi doped LDSM sample.

Table 2: Summary of Tafel and EIS curves. $E_{corr.}$ and β slope. The fit resistance and capacitance parameters of R_{sol}, R_{cor}, R_{po}, C_{cor} and C_c

Sample	$E_{corr.}$ (mV)	β (mV dec^{-1})	R_{sol} (Ω)	R_{cor} (kΩ)	R_{po} (kΩ)	C_{cor} (μF)	C_c (nF)
LDSM	39	261	5.1	3.9	19.3	2049	259
LDSM+3% Bi	-17	518	4.9	11.9	6.1	228	202
LDSM+10% Bi	-52	516	4.1	2.1	3.5	978	301

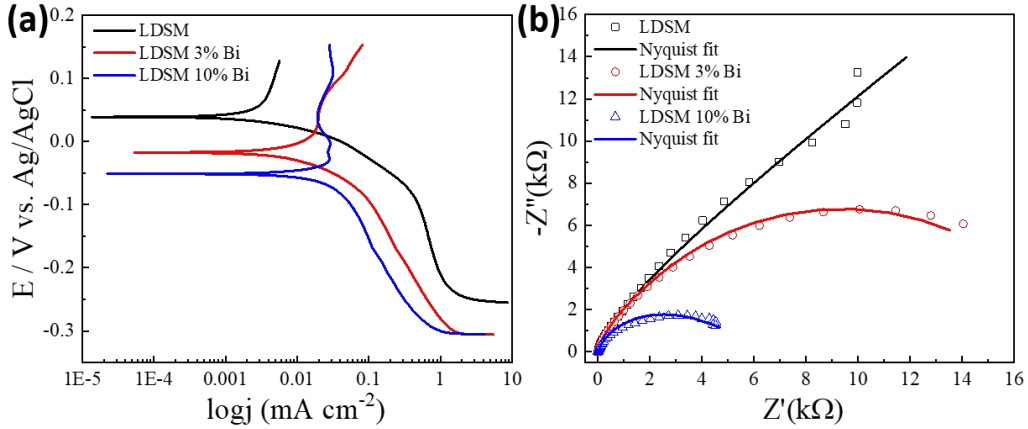

Figure 3: (a) Tafel plot and (b) EIS measurements of LDSM (black), LDSM+3% Bi (red) and LDSM+10% Bi (blue) perovskites in 1 M KOH at room temperature

4. Conclusions

In summary, we investigated the substitution of 10% Dy and 30% Sr into the A site and a small amount of Bi (x: 0, 0.03 and 0.1) added into the B site of $La_{0.60}Dy_{0.10}Sr_{0.30}Mn_{(1-x)}Bi_xO_3$ perovskites to understand the electrochemical properties for HER, OER and ORR processes. Undoped and 3% Bi doped LDSM samples exhibited poor HER activities, the effect of 10% Bi in the structure enhanced HER activities by lowering onset potential from -1.389 V to -1.036 V (vs. Ag/AgCl) and increasing specific current density at -1.4 V from -13.3 mA cm^{-2} to -121.8 mA cm^{-2}. Similarly, OER activity was also improved due to 10% Bi and onset potential and specific current density was found to be 0.758 V and 88.3 mA cm^{-2}, respectively. The large Tafel slopes indicate that the ORR mechanism is possible in the structure but at a slow rate. The substitution of 10% Bi in the structure resulted in a very high resistance of 19.3 kΩ and it reduced to a desired value of 3.5 kΩ due to ion conducting paths developed in the catalysts. So that La-based Bi-doped perovskites promise a low-cost and high-performance electrocatalytic materials candidate for regenerative fuel cells.

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