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Research Article

Sulfur Resistant Perovskite Electrocatalysts for High Temperature Applications

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Abstract

Owing to increasing demand for catalytic operations in clean and carbon negative energy systems, development of catalysts and electrocatalysts has been gaining importance and interest has been growing in mixed oxides (perovskites) that are known for their chemical and thermal stability. In the present work, some perovskite catalysts/electrocatalysts, mostly with structures ABO_3 and $A_xA'_{(1-x)}B_yB'_{(1-y)}O_3$ containing Co, Cr, La, Mo, Sr and V have been developed and studied in terms of electrical conductivity at increasing temperatures up to 1100 K. Among the samples, $La_{0.9}Sr_{0.1}Cr_{0.5}V_{0.5}O_3$, $LaSr_{0.5}V_{0.5}O_3$ and $La_{0.9}Sr_{0.1}Cr_{0.75}Co_{0.25}O_3$ had relatively higher conductivity.

Keywords: Catalyst, electrocatalyst, perovskite.

Yüksek Sıcaklıkta Uygulamalar için Kükürde Dayanıklı Perovskit Elektrokatalizörler

Öz

Temiz ve karbon negatif enerji sistemlerinde katalitik operasyonların yaygınlaşmasıyla birlikte katalizör ve elektrokatalizörlerin geliştirilmesi de önem kazanmış olup, kimyasal ve ısıl açıdan dayanıklı karışık oksitlere (perovskitler) karşı ilgi artışı sürmektedir. Bu çalışmada, temiz ve karbon negatif yaklaşımla hidrojen ve elektrik üretiminde kullanılmak üzere geliştirilmiş olan Co, Cr, La, Mo, Sr ve V içeren, genellikle ABO_3 ve $A_xA'_{(1-x)}B_yB'_{(1-y)}O_3$ yapısındaki bazı katalizör/elektrokatalizör perovskit maddeler elektriksel iletkenlik açısından 1100 K'e kadar artan sıcaklıkta incelenmiş, bunlar arasından $La_{0.9}Sr_{0.1}Cr_{0.5}V_{0.5}O_3$, $LaSr_{0.5}V_{0.5}O_3$ ve $La_{0.9}Sr_{0.1}Cr_{0.75}Co_{0.25}O_3$ bileşiklerinin daha iletken oldukları anlaşılmıştır.

Anahtar Kelimeler: Katalizör, elektrokatalizör, perovskit

1. Introduction

Global warming and environmental deterioration have been increasing with the extent of fossil fuel utilisation resulting from continual growth in global population and economy Baykara, (2018). Almost 100% of carbon dioxide (CO_2) emission is known to originate from fossil fuel based primary energy supply (~81%) and electricity production (~66%) IEA (2017).

Hydrogen as an energy carrier, Veziroglu et al (1989) and a clean critical fuel, Baykara (2005); and biomass and biocoal, Thraen et al (2016) in carbon negative electricity production via bioenergy carbon capture and storage (BECCS) approach, Newton - Cross and Gammer (2016) offer serious alternatives for bending down the steep CO_2 curve, (Figueres et al (2017) and slowing down the global temperature rise.

Presently hydrogen is mostly used as feedstocks and is generally produced from hydrocarbons and water via commercial methods. However, utilisation of hydrogen as a fuel is gradually being implemented, and additional sources of hydrogen are needed. Vastly available industrial byproducts including hydrogen sulfide (H_2S), a toxic and corrosive substance, are attracting attention among new hydrogen sources.

In recent years, parallel to the studies on solid oxide fuel cells (SOFCs) (Mori et al, 1997; Zha et al, 2005; Jiang et al, 2008; Fabbri et al, 2010) studies on electrocatalysts applicable to biogas fueled carbon fuel cells (CFCs) (Giddey et al, 2012; Gur, 2013; Coa et al, 2017) and H_2S fueled electrochemical reactors (Athanassiou, 2007; Petrov et al, 2011; Ipsakis et al, 2015) have been in progress. Next generation of SOFCs, operating below 900 K may be available in the near future (Wachsman and Lee, 2011; Fabbri et al, 2012; Gao et al, 2016).

Blocking of active sites due to sulfur (S) adsorption and development of surface reactions leading to sulfidation of oxides appear to be the main reasons causing deterioration of catalytic electrodes, Gong et al (2007). Electrocatalysts that are used as electrode materials are expected to have chemical activity, electrical conductivity; chemical and thermal stability. These properties are found in mixed oxides, generally termed as perovskites.

After $CaTiO_3$ has been the first compound identified as 'perovskite', all compounds with the ABO_3 structure have been referred to as such. The general structure of perovskites is ABX_3. A is a larger cation and B is a transition ion; X is an anion, Tejuca et al (1989). Since X is often oxygen, the representation ABO_3 is widely accepted. When one of the earth alkali elements is in position A, and a first row transition metal of the periodic table is in position B; catalytic activity is defined by the transition metal.

CFCs operating with biogas obtained from terrestial biomass can be effective in CO_2 capture. Electrochemical reactors (Uzun et al, 2015; Kraia et al, 2017) and SOFCs (Vincent et al, 2011; Li et al, 2012; Afshar et al, 2015; Uzun et al, 2016; Wachowski et al, 2018) fueled with H_2S render hydrogen or electricity production possible from a hazardous industrial byproduct.

In the present study, ABO_3 and $A_xA'_{(1-x)}B_yB'_{(1-y)}O_3$ type perovskite electrocatalysts, developed for electrodes of electrochemical reactors fueled with H_2S containing feed streams, have been investigated in terms of electrical conductivity.

The electrocatalysts may also be used as electrode materials in CFCs fueled by H_2S containing product gas obtained by gasification of biomass.

2. Materials and Method

Details about methods of synthesis, characterization, and chemical performance testing of the catalysts are given elsewhere (Guldal et al, 2015; Guldal et al, 2017; Guldal et al, 2018).

For studying electrical conductivity of the catalysts, pellets of 0.02 m diameter and 0.0005 m thickness were prepared.

Variation in the conductivity of the samples versus temperature was studied with the four point probe (FPPT) approach using the acquisition system described by Evcin et al, (2014).

3. Results and Discussion

Electrical conductivity measurements of the perovskite electrocatalysts were carried out covering the temperature range T: 425-1100 K approximately. Significant increase was observed in conductivity of electrocatalysts, proportional to increase in temperature (Figure 1, Table 1).

Table 1. Measured Values of Conductivity (σ) of Electrocatalysts

Formulation	σ (S/cm) at	
Parametre Adı	Tmin (425 K)	Tmax (1100 K)
$LaVO_3$	5.3×10^{-6}	1.6×10^{-2}
$LaSr_{0.5}V_{0.5}O_3$	2.0×10^{-6}	6.0×10^{-3}
$LaCrO_3$	1.2×10^{-5}	1.3×10^{-3}
$La_{0.9}Sr_{0.1}CrO_3$	4.1×10^{-3}	1.5×10^{-2}
$La_{0.9}Sr_{0.1}Cr_{0.5}Mo_{0.5}O_3$	2.6×10^{-5}	9.5×10^{-3}
$La_{0.9}Sr_{0.1}Cr_{0.25}Co_{0.75}O_3$	6.1×10^{-7}	2.2×10^{-3}
$La_{0.9}Sr_{0.1}Cr_{0.75}Co_{0.25}O_3$	1.8×10^{-4}	3.3×10^{-2}
$La_{0.9}Sr_{0.1}Cr_{0.5}V_{0.5}O_3$	1.0×10^{-1}	1.2×10^{-1}

S: Siemens

Physical properties of the catalysts such as crystal phases, particle sizes (μm), elemental composition (%), specific surface area (m^2/g); and chemical conversion performance (% H_2S) are available elsewhere (Guldal et al, 2015; Guldal et al, 2017; Guldal et al, 2018).

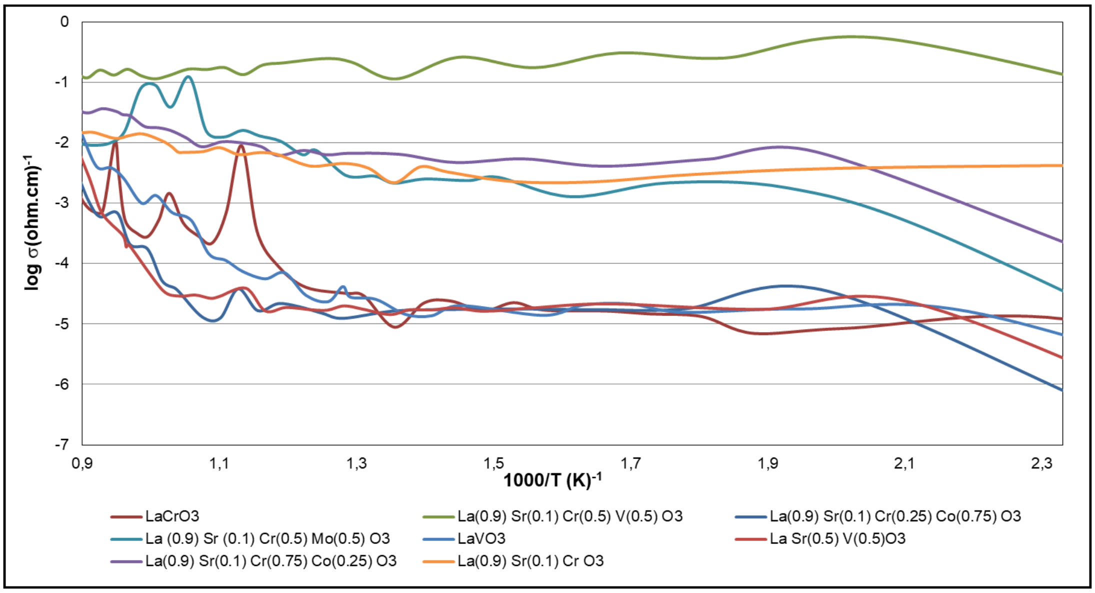

Figure 1: Electrical conductivity of $LaVO_3$, $LaSr_{0.5}V_{0.5}O_3$, $LaCrO_3$, $La_{0.9}Sr_{0.1}CrO_3$, $La_{0.9}Sr_{0.1}Cr_{0.5}Mo_{0.5}O_3$, $La_{0.9}Sr_{0.1}Cr_{0.25}Co_{0.75}O_3$, $La_{0.9}Sr_{0.1}Cr_{0.75}Co_{0.25}O_3$, $La_{0.9}Sr_{0.1}Cr_{0.5}V_{0.5}O_3$

In all perovskite electrocatalyst samples La was chosen as element A. For A', Sr was used. Cr was added as element B and B' was Co or Mo or V (Table 1).

Conductivity of samples $LaSr_{0.5}V_{0.5}O_3$, $LaVO_3$, $La_{0.9}Sr_{0.1}Cr_{0.5}Mo_{0.5}O_3$, $La_{0.9}Sr_{0.1}Cr_{0.5}V_{0.5}O_3$, $La_{0.9}Sr_{0.1}Cr_{0.75}Co_{0.25}O_3$ and $La_{0.9}Sr_{0.1}Cr_{0.25}Co_{0.75}O_3$ kept increasing up to approximately 500 K (Figure 1).

Between 500 K and 700 K conductivity appeared to be quite stabilized for almost all samples.

Afterwards, curves of samples $LaSr_{0.5}V_{0.5}O_3$, $LaVO_3$ and $La_{0.9}$ $Sr_{0.1}Cr_{0.25}Co_{0.75}O_3$ started climbing again.

Conductivity of sample $La_{0.9}Sr_{0.1}Cr_{0.5}V_{0.5}O_3$ has been higher than those of the rest throughout the temperature range, displaying a gradual decline with temperature.

Conductivity curves of $La_{0.9}Sr_{0.1}CrO_3$ and $La_{0.9}Sr_{0.1}Cr_{0.75}Co_{0.25}O_3$ displayed similar trend, climbing gradually at temperatures greater than 600 K.

Fluctuations were observed in curves of $LaCrO_3$ and $La_{0.9}Sr_{0.1}Cr_{0.5}Mo_{0.5}O_3$ after 700 K and 900 K.

Reduced system costs are anticipated with low temperature ($T \leq 900$ K) SOFCs owing to wider material choices, Wachsman and Lee (2011).

Conductivity curves of the perovskite catalysts studied in the present work (Figure 1) appear to be quite stabilized at the mentioned low temperature range ($T \leq 900$ K).

Catalysts containing Cr and V had higher conductivity both at room temperature and at the highest measurement temperature. Best results were obtained with $La_{0.9}Sr_{0.1}Cr_{0.5}V_{0.5}O_3$, followed by $LaSr_{0.5}V_{0.5}O_3$ and $La_{0.9}Sr_{0.1}Cr_{0.75}Co_{0.25}O_3$.

The effect of V addition has been observed by comparing the conductivity values, at low and high temperatures, of $La_{0.9}Sr_{0.1}Cr_{0.5}V_{0.5}O_3$ and $La_{0.9}Sr_{0.1}CrO_3$. Throughout the temperature range of measurement superior conductivity of the V containing perovskite has been demonstrated.

The effect of Cr addition has been studied through comparison of conductivity performance of Co containing perovskites $La_{0.9}Sr_{0.1}Cr_{0.75}Co_{0.25}O_3$ and $La_{0.9}Sr_{0.1}Cr_{0.25}Co_{0.75}O_3$. The sample with higher Cr content had higher conductivity. However, addition of V has been found to be more effective on conductivity. Although the sample $La_{0.9}Sr_{0.1}Cr_{0.75}Co_{0.25}O_3$ contained 1.45 times more Cr compared to $La_{0.9}Sr_{0.1}Cr_{0.5}V_{0.5}O_3$, the latter sample displayed higher conductivity, owing to presence of V.

Considering perovskites of the type $La_xSr_yCr_z(M_z)O_3$, electrical conductivity (σ) at high temperatures varied with respect to M in the order M : V > Co > Mo (Table 1).

For the electrocatalysts $LaSr_{0.5}V_{0.5}O_3$, $La_{0.9}$ $Sr_{0.1}Cr_{0.5}V_{0.5}O_3$ and $La_{0.9}$ $Sr_{0.1}Cr_{0.75}Co_{0.25}O_3$ the conductivity values were within similar range for those obtained with La and Cr containing catalysts reported in the literature (Mori et al, 1997; Jiang et al, 2008; Wachowski et al, 2018) (Table 2).

A correspondence between electrical conductivity and chemical activity (Guldal et al, 2015; Guldal et al, 2017; Guldal et al, 2018) of the perovskite electrocatalysts was not observed.

For example, although $LaCrO_3$, and its versions obtained by adding Sr and Co have shown highest chemical activity at high temperatures(Guldal et al, 2015; Guldal et al, 2017; Guldal et al, 2018); V containing perovskites had superior electrical conductivity.

Similarly, properties of the catalyst such as particle size and specific surface area (Guldal et al, 2015; Guldal et al, 2017; Guldal et al, 2018) did not seem to affect chemical activity or electrical conductivity.

Table 2: Electrical Conductivity Values of Similar Ceramic Materials

Material	T (K)	σ (S/cm)
$LaCrO_3$ (Mori et al, 1997)	373	0.6-1.0
$LaCrO_3$ (Jiang et al, 2008)	1073	0.33
$La_{0.7}Mg_{0.3}CrO_3$ (Jiang et al, 2008)	1073	2.21
$La_{0.7}Ba_{0.3}CrO_3$ (Jiang et al, 2008)	1073	2.26
$SrFe_{0.75}Mo_{0.25}O_3$ (Wachowski et al, 2018)	1073	0.005

4. Conclusion

In the present work, sulfur resistant and chemically active perovskite electrocatalysts, developed for hydrogen and/or electricity production from H_2S or biogas, have been studied in terms of electrical conductivity.

Among the samples, $La_{0.9}Sr_{0.1}Cr_{0.5}V_{0.5}O_3$, $LaSr_{0.5}V_{0.5}O_3$ and $La_{0.9}Sr_{0.1}Cr_{0.75}Co_{0.25}O_3$ were found to be the samples with higher chemical activity and electrical conductivity.

All samples have been quite stable at temperatures below 900 K.

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