DEVELOPMENT OF GADOLINIUM AND SAMARIUM DOPED CERIA ALKALI CARBONATE-COMPOSITE ELECTROLYTES FOR SOLID OXIDE FUEL CELL

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by

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Dedicated To My Beloved Family Especially My Mother.

Certificate

This is to certify that the thesis entitled "**Development of Gadolinium and Samarium Doped Ceria Alkali Carbonate-Composite Electrolytes for Solid Oxide Fuel Cell**" being submitted by **Ieeba Khan** to the Indian Institute of Technology Delhi, for fulfillment of the requirements for the award of **Doctor of Philosophy** in Chemical Engineering is a record of bona fide research work carried out by her. She has worked under my supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of the thesis. The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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Abstract

The growing energy demand in the world has led to ruthless environment degradation due to excessive use of fossil fuels. This necessitates an approach towards the search and development for new alternative energy sources which are clean and have near zero environmental impacts. Development of solid oxide fuel cell (SOFC) run on hydrogen obtained from renewable source as an energy conversion device perfectly fits into this requirement. Electrolytes being the main source of resistance in the solid oxide fuel cells govern the operating temperature of the solid SOFC.

In this thesis, doped ceria composited with alkali or alkaline carbonates are being suggested as promising electrolyte material for use in intermediate temperature SOFC (IT-SOFC). Various compositions of unary, binary, and ternary gadolinium doped ceria (GDC)-carbonate electrolytes are prepared using (Na_2, Li_2, K_2, Sr)-CO_3 and GDC using solid-state route. In the unary GDC-carbonate composite electrolytes, highest ionic conductivity is shown by 25 wt% Li_2CO_3-GDC electrolyte (0.077 S cm^{-1} at 600 °C). The ternary carbonate composite mixture of 25 wt% $(LiNaK)_2CO_3$-GDC exhibits higher ionic conductivity (0.29 S cm^{-1} at 600 °C) than binary and unary carbonate electrolytes. At 600 °C, the peak power density for the cell of ternary carbonate, 25 wt% $(LiNaK)_2CO_3$-GDC electrolyte and binary carbonate, 25 wt% $(LiNa)_2CO_3$-GDC electrolyte is 224 mW cm^{-2} (at 555 mA cm^{-1}) and 180 mW cm^{-2} (at 417 mA cm^{-1}), which would enable them to be used as electrolytes in low temperature SOFC.

Thermal stability and sintering of $(LiNa)_2CO_3$ in GDC is an issue due to leaching of carbonate at higher temperature. Infiltrated $(LiNa)_2CO_3$ in pre-formed GDC electrolyte matrix sintered at 1450 °C shows enhanced stability and strength. Porous matrix of GDC is fabricated by sintering

at 1450 °C and subsequently the prefabricated matrix is melt infiltrated with mixture of $(LiNa)_2CO_3$ (1:1 wt. ratio). Physical characterisations of the composite electrolytes are analyzed using X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy, fourier transform infrared spectroscopy and thermal gravimetric analysis. The ionic conductivity of melt infiltrated 30 wt% $(LiNa)_2CO_3$-GDC composite electrolyte is 0.15 S cm^{-1} at 600 °C. The bilayer performance of melt infiltrated composite electrolyte is better (192 mW cm^{-2} at 485 mA cm^{-2}) than that prepared by solid-state method (42 mW cm^{-2} at 106 mA cm^{-2}) at 700 °C. The i-R compensated peak power density of 573 mW cm^{-2} (953 mA cm^{-2}) is observed at 750 °C in 30 wt% $(LiNa)_2CO_3$-GDC melt infiltrated composite electrolyte. The morphology, thermal analysis and electrochemical studies of melt infiltrated composite electrolytes reveals better performance due to well-sintered stable structure.

Apart from GDC, samaria doped ceria (SDC) electrolyte composited with carbonate is equally promising to be IT-SOFC electrolyte. Optimization study for the best carbonate wt % composition in doped ceria is carried out using electrolyte compositions of 20, 25, 30, 35, 45 wt% $(LiNaK)_2CO_3$-SDC. The best ionic conductivity is obtained for 45 wt% $(LiNaK)_2CO_3$-SDC composite electrolyte (0.72 S cm^{-1} at 600 °C) followed by the 35 wt% $(LiNaK)_2CO_3$–SDC composite electrolyte (0.55 S cm^{-1} at 600 °C). The symmetrical cell of the 35 wt% $(LiNaK)_2CO_3$-SDC composite electrolyte with lanthanum strontium cobalt ferrite (LSCF) electrode in air gives an area specific resistance of 0.155 Ω cm^2 at 500 °C. The maximum power density of the fuel cell using 35 wt% $(LiNaK)_2CO_3$-SDC composite electrolyte, composite NiO anode and composite LSCF cathode is found to be 801 mW cm^{-2} at 550 °C.

सार

दुनिया में ऊर्जा की बढ़ती मांग के कारण जीवाश्म ईंधन के अत्यधिक उपयोग के कारण पर्यावरण के खराब होने की संभावना बढ़ गई है। यह नए वैकल्पिक ऊर्जा स्रोतों के लिए खोज और विकास के लिए एक दृष्टिकोण की आवश्यकता है जो स्वच्छ हैं और शून्य पर्यावरणीय प्रभावों के पास हैं। नवीकरणीय स्रोत से प्राप्त हाइड्रोजन पर ठोस ऑक्साइड ईंधन सेल (SOFC) का विकास एक ऊर्जा रूपांतरण उपकरण के रूप में पूरी तरह से इस आवश्यकता में फिट बैठता है। इलेक्ट्रोलाइट्स ठोस ऑक्साइड ईंधन कोशिकाओं में प्रतिरोध का मुख्य स्रोत होने के नाते ठोस एसओएफसी के संचालन तापमान को नियंत्रित करते हैं।

इस थीसिस में, क्षार या क्षारीय कार्बोनेट के साथ कंपोज की गई डोपिया को मध्यवर्ती तापमान SOFC (IT-SOFC) में उपयोग के लिए होनहार इलेक्ट्रोलाइट सामग्री के रूप में सुझाया जा रहा है। यूनिरी, बाइनरी और टर्नरी गैडोलिनियम डोप्ड सेरिया (जीडीसी) -कार्बोनेट इलेक्ट्रोलाइट्स की विभिन्न रचनाएं ठोस-राज्य मार्ग का उपयोग करके (Na_2, Li_2, K_2, Sr) -CO_3 और GDC का उपयोग कर तैयार की जाती हैं। संयुक्त जीडीसी-कार्बोनेट मिश्रित इलेक्ट्रोलाइट्स में, उच्चतम आयनिक चालकता 25 wt% Li_2CO_3-GDC इलेक्ट्रोलाइट (0.077 S cm^{-1} at 600 °C). द्वारा दिखाया गया है। 25 wt% (LiNaK) $_2CO_3$-GDC का टर्नरी कार्बोनेट मिश्रित मिश्रण बाइनरी और अनार्य कार्बोनेट इलेक्ट्रोलाइट्स की तुलना में उच्च आयन चालकता (0.29 S cm^{-1} at 600 °C) प्रदर्शित करता है। 600 ° C पर, टर्नरी कार्बोनेट की सेल के लिए शिखर शक्ति घनत्व, 25 wt% (LiNaK) $_2CO_3$-GDC इलेक्ट्रोलाइट और बाइनरी कार्बोनेट, 25 wt% (LiNa) $_2CO_3$-GDC इलेक्ट्रोलाइट 224 mW cm^{-2} (पर 555 mA cm^{-1}) और 180 mW cm^{-2} (पर 417 mA cm^{-1}), जो उन्हें कम तापमान SOFC में इलेक्ट्रोलाइट्स के रूप में उपयोग करने में सक्षम करेगा।

जीडीसी में थर्मल स्थिरता और सिंटरिंग (LiNa) $_2CO_3$ उच्च तापमान पर कार्बोनेट की लीचिंग के कारण एक मुद्दा है। पहले से गठित GDC इलेक्ट्रोलाइट मैट्रिक्स में घुसपैठ किए गए (LiNa) $_2CO_3$1450 डिग्री सेल्सियस पर sintered बढ़ाया स्थिरता और ताकत से पता चलता है। GDC का छिद्रपूर्ण मैट्रिक्स 1450 डिग्री सेल्सियस पर sintering द्वारा गढ़ा गया है और बाद में पूर्वनिर्मित मैट्रिक्स (LiNa) $_2CO_3$ (1: 1 wt। अनुपात) के मिश्रण के साथ घुसपैठ की जाती है।

कम्पोजिट इलेक्ट्रोलाइट्स की शारीरिक विशेषताओं का विश्लेषण एक्स-रे विवर्तन, स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी, एनर्जी डिस्पर्सिव स्पेक्ट्रोस्कोपी, फूरियर ट्रांसफॉर्म इन्फ्रारेड स्पेक्ट्रोस्कोपी और थर्मल ग्रेविमिट्रिक विश्लेषण का उपयोग करके किया जाता है। पिघल की आयनिक चालकता 30 wt% (LiNa) $_2CO_3$ समग्र इलेक्ट्रोलाइट 0.15 S cm^{-1} at 600 °C पर घुसपैठ की है। पिघले हुए मिश्रित मिश्रित इलेक्ट्रोलाइट का बाइलियर प्रदर्शन 700 ° C पर ठोस अवस्था विधि (42 mW cm^{-2} पर 106 mA cm^{-2}) द्वारा तैयार की तुलना में बेहतर (192 mW cm^{-2} पर 485 mA cm^{-2}) है। 573 mW cm^{-2} (953 mA cm^{-2}) का i-R क्षतिपूर्ति शिखर घनत्व 30 wt% $(LiNa)_2CO_3$-GDC पिघल घुसपैठ समग्र इलेक्ट्रोलाइट में 750 ° C पर मनाया जाता है। पिघल घुसपैठ मिश्रित इलेक्ट्रोलाइट्स की आकृति विज्ञान, थर्मल विश्लेषण और विद्युत रासायनिक अध्ययन अच्छी तरह से पापी स्थिर संरचना के कारण बेहतर प्रदर्शन का पता चलता है।

जीडीसी के अलावा, कार्बोनेट के साथ कंपोजिट किए गए सेमरिया डोपेड सेरिया (एसडीसी) आईटी-एसओएफसी इलेक्ट्रोलाइट के समान ही आशाजनक है। डोप्ड सेरिया में सर्वश्रेष्ठ कार्बोनेट wt% संरचना के लिए अनुकूलन अध्ययन 20, 25, 30, 35, 45 wt% $(LiNaK)_2CO_3$-SDC की इलेक्ट्रोलाइट रचनाओं का उपयोग करके किया जाता है। सबसे अच्छी आयनिक चालकता 45 wt% $(LiNaK)_2CO_3$-SDC समग्र इलेक्ट्रोलाइट (600 डिग्री सेल्सियस पर 0.72 S सेमी -1) 35 wt% $(LiNaK)_2CO_3$-SDC समग्र इलेक्ट्रोलाइट (0.55 S cm^{-1}) के लिए प्राप्त की जाती है। 600° C)। हवा में लैंथेनम स्ट्रोंटियम कोबाल्ट फेराइट (LSCF) इलेक्ट्रोड के साथ 35 wt% $(LiNaK)_2CO_3$-SDC कम्पोजिट इलेक्ट्रोलाइट का सममित सेल 500 ° C पर 0.155 Ω cm^2 का एक क्षेत्र विशिष्ट प्रतिरोध देता है। 35 wt% $(LiNaK)_2CO_3$-SDC समग्र इलेक्ट्रोलाइट, मिश्रित NiO एनोड और मिश्रित LSCF कैथोड का उपयोग करके ईंधन सेल की अधिकतम शक्ति घनत्व 550 डिग्री सेल्सियस पर 801 mW सेमी -2 पाया जाता है।

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