

Análisis de materiales catódicos de estructura perovskita para celdas de combustible de óxido sólido, sofc's

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Las celdas de combustible convierten directa y eficientemente la energía química de un combustible en energía eléctrica. De los diversos tipos de celdas de combustible, las de óxido sólido (SOFC), combinan las ventajas en generación de energía ambientalmente benigna con la flexibilidad del combustible. Sin embargo, la necesidad de elevadas temperaturas de funcionamiento (800-1000°C) se ha traducido en altos costos y grandes retos en relación a la compatibilidad para los materiales catódicos. Como consecuencia, se han realizado importantes esfuerzos en el desarrollo de celdas SOFC de temperatura intermedia (500-700°C). Un obstáculo clave para su funcionamiento en este rango de temperatura, es la limitada actividad de los tradicionales materiales catódicos para la reducción electroquímica de oxígeno. En este artículo, se analiza el progreso de los últimos años en cátodos para celdas SOFC de estructura perovskita (ABO_3), más eficientes que el tradicionalmente usado $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (LSM) o $(\text{La}, \text{Sr})\text{CoO}_3$. Tal es el caso de los conductores mixtos (MIEC) de estructura doble perovskita ($\text{AA}'\text{B}_2\text{O}_{5+\delta}$) utilizando diversos elementos de dopaje como La, Sr, Fe, Ti, Cr, Sm, Co, Cu, Pr, Nd, Gd, Dy, Mn, entre otros, que puedan mejorar el rendimiento operacional de los materiales catódicos existentes, promoviendo el desarrollo de diseños optimizados de celdas SOFC de temperatura intermedia.

Descriptores: Cátodos de estructura perovskita; conductividad eléctrica; celda de combustible de óxido sólido (SOFC).

Fuel cells directly and efficiently convert the chemical energy of a fuel into electrical energy. Of the various types of fuel cells, the solid oxide (SOFC), combine the advantages in environmentally benign energy generation with fuel flexibility. However, the need for high operating temperatures (800 - 1000°C) has resulted in high costs and major challenges in relation to the compatibility the cathode materials. As a result, there have been significant efforts in the development of intermediate temperature SOFC (500 - 700°C). A key obstacle for operation in this temperature range is the limited activity of traditional cathode materials for electrochemical reduction of oxygen. In this article, the progress of recent years is discussed in cathodes for SOFC perovskite structure (ABO_3), more efficient than the traditionally used $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (LSM) or $(\text{La}, \text{Sr})\text{CoO}_3$. Such is the case of mixed conductors (MIEC) double perovskite structure ($\text{AA}'\text{B}_2\text{O}_{5+\delta}$) using different doping elements as La, Sr, Fe, Ti, Cr, Sm, Co, Cu, Pr, Nd, Gd, dy, Mn, among others, which could improve the operational performance of existing cathode materials, promoting the development of optimized intermediate temperature SOFC designs.

Keywords: Perovskite cathode structure; electrical conductivity; solid oxide fuel cell (SOFC).

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1. Introducción

En los últimos años se ha desarrollado de forma rápida, la tecnología de celdas de combustible así como varios tipos de celdas en función de la aplicación requerida (Tabla I). De los diversos tipos disponibles de celdas de combustible, la celda de combustible de óxido sólido, SOFC (Fig. 1), ha demostrado ser una excelente alternativa para diferentes aplicaciones, desde equipos portátiles utilizados en transportación con potencia de 1 kW, hasta plantas estacionarias con potencias mayores a 100 kW y fabricadas por diversas compañías como Siemens Westinghouse [1,2]. Recientemente, una planta semejante, localizada en los Países Bajos, ha completado con éxito dos años en operación, suministrando de energía a la red nacional, lo cual ha sido el mayor logro de una celda SOFC en operación. Sin embargo, y aunque las celdas SOFC representan atractivas alternativas a las fuentes convencionales de energía, sufren de algunas deficiencias tecnológicas debi-

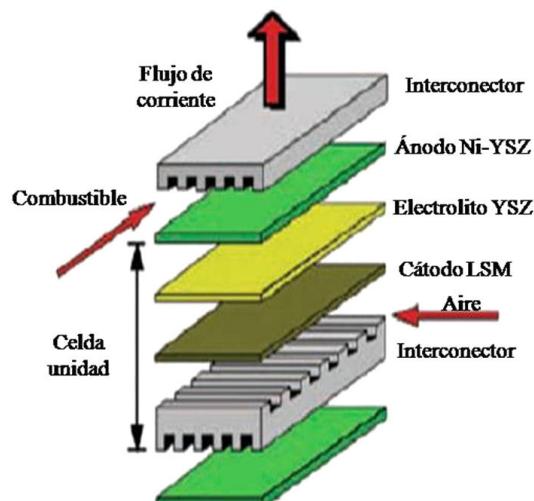


FIGURA 1. Diseño planar de una celda de combustible de óxido sólido, SOFC..



Characterization and HDS performance of sulfided CoMoW catalysts supported on mesoporous Al-SBA-16 substrates



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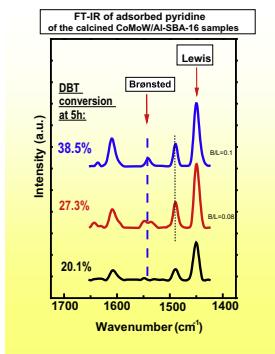
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HIGHLIGHTS

- CoMoW sulfide catalysts supported on mesoporous Al-SBA-16 silica are active in HDS of DBT.
- The CoMoW/SBA-16 catalyst modified with a largest amount of Al displayed the largest HDS activity.
- Al-incorporation on SBA-16 by direct synthesis method results in formation of Brønsted and Lewis acid sites.
- Bifunctionality of CoMoW/Al-SBA-16 catalysts improves their performance for HDS of DBT.

GRAPHICAL ABSTRACT

Al incorporated into SBA-16 led to both Brønsted and Lewis acidity that is beneficial for HDS reaction.



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ABSTRACT

In this work, the catalytic activity of ternary Co–Mo–W/Al-SBA-16 systems was investigated in the reaction of hydrodesulfurization (HDS) of dibenzothiophene (DBT) performed in a batch reactor at 350 °C and total H₂ pressure of 33.8 bar. The synthesized materials were characterized by a variety of techniques (chemical analysis, N₂ adsorption–desorption isotherms, XRD, TPR, TPD-NH₃, FTIR of adsorbed pyridine, DRS-UV-vis, HRTEM and XPS). By applying the direct synthesis method, high surface area substrates with Al³⁺ incorporated into the silica framework. The activity results indicate that all CoMoW/Al-SBA-16 catalysts were active in the HDS of DBT, the largest activity was found in the catalyst with the highest Al-content. This behavior was explained in terms of its largest specific area and good dispersion of the metal sulfide phases having average size of 3.3 nm (from HRTEM). Moreover, FT-IR spectroscopic study of adsorbed pyridine indicated Al incorporation into a SBA-16 substrate produces both Brønsted and Lewis acidities, which are beneficial for the HDS of DBT. All catalysts showed a high selectivity towards biphenyl indicating that HDS of DBT reaction proceeds mainly via direct desulfurization (DDS) reaction pathway.

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Short Communication

Experimental methodology to calculate the local relative light intensity in heterogeneous TiO₂/UV-A photocatalytic reactors



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ABSTRACT

In the field of heterogeneous photocatalysis, catalyst concentration is one of the main parameters that restricts light availability, specifically in photocatalytic annular slurry reactors design. Therefore, data that describes the dependence of energy on both, distance and catalyst concentration is needed. This paper proposes the local relative light intensity (LRLI) as a quantity that represents the residual energy on radial distance. Experimental measurements of LRLI were made from 0 mm to 25 mm, using two commercial TiO₂ powders in a wide range of concentration (200 to 1000 mg/L). Results show that residual energy was less than 80% at 6 mm from the source, for both catalysts in all concentrations. Furthermore, a forward-scattered behavior was detected, the LRLI profiles (LRLI vs radial distance) followed an exponential decay model. All profiles were correlated as a catalysts concentration function. Information obtained was used to develop a methodology to calculate the LRLI values at any radial distance for a settle catalyst concentration. The calculated values of LRLI approaches real data with a relative local accumulated error less than 10% for both catalysts. This methodology may be applied to calculate the energy available in any TiO₂/UV-A annular slurry system.

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1. Introduction

The heterogeneous photocatalysis TiO₂/UV-A is one of the advanced oxidation processes used to remove toxic, recalcitrant and colored pollutants in water. The ultraviolet light (UV-A) has enough energy to induce an excited state in semiconductor (TiO₂) and promotes the creation of electron–hole pairs, this allows the reactive oxygen species production (e.g. hydroxyl radicals) (Liao et al., 2013). These compounds are highly reactive with organic pollutants until mineralization is reached (Chong et al., 2010; Akpan and Hameed, 2009; Nakata

and Fujishima, 2012). The light dependence of photocatalytic process has led to several reactor configurations and the efficiency varies from one system to another (McCullagh et al., 2011). The annular slurry photoreactor is widely used (Moreira et al., 2011; Yang et al., 2005; Zekri and Colbeau-Justin, 2013; Ballari et al., 2008; Imoberdorf et al., 2008), it is considered the most efficient configuration because it takes advantage of emitted radiation, increasing process effectiveness (De Las et al., 2005). Nevertheless, the efficiency of this kind of configuration is restricted by energy available along suspended media. Some efficiency definitions (e.g. photonic efficiency),

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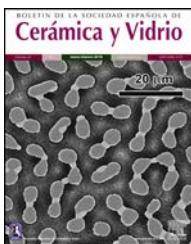
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Impregnación de la perovskita $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ como ánodo en celdas SOFC



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RESUMEN

Se han sintetizado a través del método sol-gel, y caracterizado por varias técnicas, nuevos compósitos tipo perovskita de $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM), utilizando cobre (XCu; X = 25, 35 y 45%) como aditivo formador del cermet LSCM + Cu para utilizarse como ánodos alternativos en celdas de combustible de óxido sólido de temperatura intermedia (IT-SOFC). Se confirma por difracción de rayos X (XRD) la formación de fase de los cermets LSCM-Cu. La conductividad eléctrica obtenida desde temperatura ambiente hasta 800 °C indica la presencia de 2 tipos de comportamiento tanto semiconductor como metálico. Cuando la concentración de Cu fue del 25 y del 35%, el comportamiento que dominó fue del tipo semiconductor. La determinación de los coeficientes de expansión térmica (TEC) mostró una dependencia lineal inversamente proporcional a la concentración de Cu. Nuestros resultados de conductividad eléctrica, análisis morfológico y TEC sugieren que los ánodos con 25 y 35% de Cu tienen la mayor posibilidad para aplicarse en las celdas tipo SOFC-IT.

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Impregnation of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta} + \text{Cu}$ perovskite as the anode for SOFCs

ABSTRACT

New types of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) perovskite composites with the addition of copper(Cu), XCu (X = 25, 35 and 45%) as forming additive, were synthesized via the sol-gel method as alternative anodes for intermediate-temperature solid oxide fuel cells (IT-SOFCs) and characterized by several techniques. Phase formation of the LSCM-Cu cermets was confirmed by X-ray diffraction (XRD). Electrical conductivity was obtained from room temperature to 800 °C, indicating the presence of two types of behaviors: both semiconductor and metal. When the concentration of Cu was 25 and 35%, the dominant behavior was the semiconductor type. The thermal expansion coefficient (TEC) determined was linearly inversely proportional to the concentration of Cu. The results of electrical conductivity, TEC,

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**LA NECESIDAD DE INCORPORAR EL HIDRÓGENO COMO POTENCIAL
FUENTE ALTERNA DE ENERGÍA EN LA LEGISLACIÓN MEXICANA**

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Synthesis of iron sulfide films through solid-gas reaction of iron with diethyl disulfide

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