



Editorial

Catalysis for Low-Temperature Fuel Cells

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1. Introduction

Today, the development of active and stable catalysts still represents a challenge to be overcome in the research field of low-temperature fuel cells. Operation at low temperatures offers great advantages, such as quick start-up and longer stability, but demands the utilization of highly active catalysts to reduce the activation energy of the electrochemical reactions involved in the electrodes, and thus obtain practical performances and high efficiencies. At present, the best-performing catalysts in low-temperature fuel cells are based on highly-dispersed Pt nanoparticles [1]. However, these present several drawbacks, such as high cost, limited earth resources, sensitivity to contaminants, low tolerance to the presence of alcohols, and instability due to carbon support electrochemical oxidation and Pt dissolution [2–4].

In the search for alternative catalysts, researchers have pursued several strategies: increase of the utilization of Pt catalysts by means of novel structures (metal/support) [5,6]; alloying with earth-abundant and cost-effective transition metals [7–9]; new carbon and non-carbon supports [10–13]; cheaper platinum-group-metals like Pd [14–16]; non-platinum-group metals catalysts (Fe-N-C, Co-N-C, etc.) [17–19]; among others.

This Special Issue (SI) is intended to cover the most recent progress in advanced electro-catalysts, from the synthesis and characterization to the evaluation of activity and degradation mechanisms, in order to gain insights towards the development of high-performing fuel cells.

2. This Special Issue

This SI includes 10 high-quality contributions related to recent works in catalysis for low-temperature fuel cells. It comprises four review papers covering aspects such as palladium-based catalysts, non-precious catalysts, the catalyst/support interaction, and the effects related to cell reversal. Six full research articles are also included, dealing with several strategies aimed to maximize catalytic activity through innovative and advanced synthesis techniques.

Calderón-Gómez et al. reviewed the progress for the last ten years concerning palladium-based catalysts as electrodes for direct methanol fuel cells (DMFCs) [20]. Palladium, although belonging to the precious platinum group metals, is cheaper and more abundant than platinum. In the review, Pd catalysts are categorized in two typologies: carbon-supported and non-carbon-supported palladium alloys. Recent studies of these catalysts for the methanol oxidation reaction (MOR) and for the oxygen reduction reaction (ORR) point to a great potential of palladium-based catalysts for replacing platinum as active phase in the electrodes of DMFCs. The alloying of Pd with appropriate metals appears to be crucial for increasing the catalytic activity. It is also concluded that carbon supports aid in dispersing noble metal nanoparticles while favoring the electronic transference, and non-carbon supports (perovskites, titanium oxide, tungsten carbide, etc.) provide modifications in the electronic structure of Pd active sites.

In the review article of Mora-Hernández et al., some of the best-performing catalyst formulations are covered, involving precious and non-precious catalysts [21]. It is divided in three main sections concerning the design of catalytic materials (precious metals, chalcogenides, and non-precious catalysts), the fuel cell reactions of interest (hydrogen oxidation and oxygen reduction), and the important role of catalyst supporting materials (low and high graphitic carbon as well as oxide and composites), and finally a review of micro fuel cells. Novel synthetic routes including photo-deposition, the use of ligands or chalcogenides appear as promising strategies to improve the activity and stability of catalysts for ORR through strong metal-support interactions, nanoalloys with some transition metals, and enhanced tolerance to the presence of small organic molecules like methanol.

Non-precious catalysts are becoming increasingly attractive from sustainable and economical points of view. Brouzougou et al. review the most recent achievements in novel carbon materials for the oxygen reduction in alkaline environment [22]. In particular, the attention is focused on three-dimensional hybrid catalysts, of which nitrogen-doped reduced graphene oxides present the most promising electrochemical activity but short stability over time. Dual-doped ORR catalysts based on mesoporous carbon structures with co-doping metals embedded throughout the carbon matrix are also reviewed, with great prospects in terms of activity and still room for improving stability. More recent three-dimensional interconnected structures in which two metals interact with a graphene-based support are also reviewed, concluding that the main challenge remains to be the enhancement of stability.

The fourth review paper by Qin et al. regards the effects of fuel cell reversal (i.e., anode voltage being superior to cathode and demanding energy rather than supplying it) on irreversible damage: causes, consequences and mitigation strategies [23]. Carbon support corrosion, catalyst and sinter agglomeration, and membrane degradation can permanently harm the fuel cell operation. Two main strategies can be adopted: material modification to resist cell reversal conditions and proper system management. The proper choice of catalyst features for high activity appears as a crucial parameter in addition to operating conditions and carbon supports to mitigate the cell damaging.

This SI also includes six full research papers. Four of them deal with Pt-based catalysts, highlighting the importance that this noble metal still represents in this field. Three of these papers concern the MOR. At the anode of DMFCs, the latter is still a sluggish reaction conditioning the performance of the global cell together with the ORR. Caballero-Manrique et al. investigated the effect of Cu electrodeposition time of PtCu and PtRuCu catalysts [24]. They observed an optimum charge associated with Cu electrodeposition, together with Ru-decoration, to maximize carbon monoxide and methanol oxidation electro-catalytic activity. The enhancement was attributed to the formation of a Pt shell completely covering the Cu core, leading to maximum electrochemical surface areas. The works of Xu et al. and Wang et al. regard the utilization of graphene-supported Pt-based catalysts for the electro-oxidation of methanol [25,26]. Xu et al. propose a one-pot synthetic method to produce composites based on Pt and graphene mediated by a template (polyamidoamine or chitosan) [25]. The use of templates leads to a stronger interaction between Pt and the support resulting in improved MOR activity, whereas the addition of a second metal in Pt-Ag catalysts supported on graphene also resulted in improved performance for the MOR [26], particularly in the presence of UV irradiation. Qayyum et al. explored the synthesis of Pt nanoparticles by pulsed laser deposition [27]. This preparation technique permits the synthesis of high-performing electrodes characterized by low loading of platinum for the ORR, being demonstrated at the cathode of a single cell.

Among Pt-free related papers, the work of Feng et al. describes the fabrication of PdAg-nanochain-based catalysts for the ethanol oxidation reaction (EOR) [28]. The use of a simple one-step hydrothermal method with dimethyl formamide resulted in a particular nanochain structure with enhanced EOR activity when compared to Pd/C catalysts in alkaline medium. They associated this to the improved electrochemical surface area of PdAg nanoparticles. Regarding the efforts for completely removing platinum-group metals in the catalysts, new catalyst structures are being pursued with great results. In this SI, the development of active and stable non-precious metal catalyst for the ORR was

reported by Park et al. [29]. They reported a novel $\text{Fe}_x\text{N}_y/\text{NC}$ nanocomposite obtained by pyrolysis of carbon black and an iron precursor in ammonia atmosphere. They report the essential role of Fe_3N species as the active site for the ORR, obtaining excellent activity and stability.

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