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Editorial

Electrocatalysts for Energy Conversion and Storage Devices

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1. Introduction

Energy's efficient conversion and storage are closely correlated to the development of electrochemical energy technologies, such as fuel cells, batteries, electrolyzers, etc. Such devices are claimed to dominate the future sustainable energy economy. Yet, the practical efficiencies must be boosted before many of the aforementioned technologies become viable for large-scale use. In particular, more active, stable, and economically feasible catalysts must be developed for the electrocatalytic processes occurring at practical electrodes of the cells. In this context, the research and development of efficient catalysts are vital to reaching this target. This Special Issue is intended to present and discuss the most recent advances and developments in heterogeneous catalysis for application in electrochemical energy conversion and storage devices.

2. This Special Issue

This Special Issue includes 13 high-quality, original articles related to advances in electrocatalysts/electrode development for energy conversion and storage devices or their physicochemical/electrochemical characterization. Most of these papers deal with fuel cell electrocatalysts, mainly addressing the oxygen reduction reaction (ORR) process. Shen et al. [1] explored self-supported Fe-N-C materials, as alternatives to Pt, for the ORR. The catalysts were prepared by the pyrolysis of dual precursors, including EDTA ferric sodium (EDTAFeNa) and melamine (MA), followed by acid-leaching and final annealing. Results showed onset (E_{onset}) and half-wave ($E_{1/2}$) potentials for the ORR of 0.97 and 0.84 V vs. RHE, respectively, with predominantly a four-electron pathway, similar to the state-of-the-art Pt/C catalyst. Dembinska et al. [2] investigated hybrid systems composed of reduced graphene-oxide-supported platinum and multiwalled carbon-nanotube-supported iridium (both noble metals utilized at low loadings) for the ORR using the rotating ring-disk electrode (RRDE). The addition of iridium produced an enhancement of the electrocatalytic activity, together with a reduction of hydrogen peroxide production. In the work of Mazzapioda et al. [3], a nonstoichiometric calcium titanate $CaTiO_{3-\delta}$ (CTO) was synthesized and used as an oxygen reduction reaction co-catalyst (together with Pt/C) in direct methanol fuel cells (DMFCs). The presence of the CTO additive promoted the oxygen reduction reaction (ORR) due to the presence of oxygen vacancies as available active sites for oxygen adsorption in the lattice. The increase in power density obtained with the CTO-based electrode, compared with the benchmark Pt/C, was more than 40% at 90 °C, reaching a maximum power density close to 120 mW cm^{-2}. Yuan et al. [4] synthesized graphene-like mesoporous carbon sheets with point defects as oxygen reduction/hydrogen evolution bifunctional electrocatalysts by a bubble templating method. They showed excellent ORR performance, with an onset potential of 740 mV and a diffusion-limiting current density of 4.07 mA cm^{-2}. The catalyst was also investigated for the hydrogen evolution reaction showing an overpotential of about −453 and −378 mV at 10 mA cm^{-2} in both alkaline and acidic media.

The ORR is a key process also in solid oxide fuel cells (SOFCs). In this context, Zeng et al. [5] reported a Zn-doped perovskite oxide $Ba_{0.5}Sr_{0.5}(Co_{0.8}Fe_{0.2})_{0.96}Zn_{0.04}O_{3-\delta}$

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(BSCFZ) as the SOFC cathode, which exhibited much higher electrocatalytical activity than $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) for the ORR. An increase in maximum power density by 35% in comparison with the BSCF cathode was recorded in a single cell at 750 °C, attributed to a better balance of oxygen vacancies, surface electron transfer, and ionic mobility as promoted by the low-valence Zn^{2+} doping.

Degn Jensen et al. [6] fabricated thin-film PtxGd electrocatalysts with different stoichiometry using a co-sputter deposition technique. These materials showed great oxygen reduction activity improvement over pure Pt. Co-sputtered Pt_5Gd and $Pt_{7.5}Gd$ thin films were also investigated using X-ray absorption spectroscopy, revealing the importance of forming alloys with specific stoichiometry and supporting the need of forming compressively strained Pt overlayers in order to achieve optimum catalytic performances.

Pushkarev et al. [7] used a polyol method to synthesize Pt/C and Pt/SnOx/C catalysts. They were investigated in a rotating disk electrode (RDE) for the ethanol oxidation reaction (EOR). The addition of SnOx to Pt produced a significant increase of the catalyst activity for EOR and ethanol utilization.

Another study regarding catalysts for the ethanol electro-oxidation in alkaline direct ethanol fuel cells was presented by Berretti et al. [8]. Quantifying the oxidation of fuel cell catalysts (in the present case based on Pd nanoparticles) is a task of tremendous importance to design mitigation strategies that extend the service life of catalysts and devices. In their work, the authors successfully demonstrated the application of Fixed Energy X-ray Absorption Voltammetry (FEXRAV) to the quantification of the speciation of palladium in situ, for a given sample with a defined particle distribution.

Recently, polymer electrolyte fuel cells with alkaline anion exchange membranes (AAEMs) have gained tremendous attention due to the advantages of using non-noble metal catalysts. Sebastián et al. [9] examined the preparation procedures for electrodes to be used in anion exchange membrane fuel cells using a commercial Fumasep® FAA-3 membrane and a commercial ionomer of the same nature (Fumion), both from Fumatech GmbH. The anion exchange procedure, the ionomer concentration in the catalytic layer, and also the effect of membrane thickness were analyzed in their paper.

The hydrogen evolution reaction (HER), in the absence and presence of light, on graphite paste (Gr) electrodes including N-octylpyridinium hexafluorophosphate ($OPyPF_6$) ionic liquid (IL) as binder and modification with Co-octaethylporphyrin (Co), was investigated by Gidi et al. [10]. Through gas chromatography, it was determined that the graphite paste electrode in the presence of ionic liquid and porphyrin (Gr/IL/Co) presented a high turnover number (TON; 6342 and 6827 in presence of light) in comparison with similar systems reported in the literature.

Lo Vecchio et al. [11] fabricated a tandem photoelectrochemical cell (PEC) consisting of an anionic solid polymer electrolyte membrane (gas separator) clamped between an n-type Fe_2O_3 photoanode and a p-type CuO photocathode. The semiconductors were deposited on fluorine-doped tin oxide (FTO) transparent substrates and the cell was investigated for the water splitting process. Furthermore, a NiFeOx cocatalyst was deposited on the hematite photoanode surface and investigated as a surface catalytic enhancer in order to improve the oxygen evolution reaction (OER) kinetics.

Choi et al. [12] synthesized an activated carbon (AC) with various weight ratios of manganese dioxide (MO) through a simple hydrothermal approach. The composite materials were electrochemically investigated for their potential application in supercapacitors. They exhibited specific capacitance of 60.3 F g^{-1} at 1 A g^{-1}, as well as stable cycle performance and 99.6% capacitance retention over 5000 cycles.

In the last article of this special issue, Yu et al. [13] employed a silver (Ag) foam as a catalytic electrode for the electrochemical reduction of CO_2 in aqueous solution to produce different syngas ratios (H_2:CO).

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