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Innovative carbon-free low content Pt catalyst supported on Mo-doped titanium suboxide (Ti_3O_5-Mo) for stable and durable oxygen reduction reaction

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ABSTRACT

Recently the use of titanium oxide and titanium suboxides (Magnéli phases) has been extensively investigated as an alternative catalyst support to carbon-based materials for the oxygen reduction reaction in low-temperature fuel cells. In this study, a 15 wt.% Pt-based catalyst was developed on a unique, stable mix of titanium suboxides, with a prevailing of the Ti_3O_5 phase, doped with Mo, as a Ti_3O_5-Mo carbon-free support and compared to a commercial 20 wt.% Pt/C (E-TEK). The Pt/Ti_3O_5-Mo catalyst exhibits excellent electroactivity and stability toward the ORR, reaching a performance of 73.3 mA mg^{-1}, slightly more than the double of the commercial Pt/C, with a current density of 1.1 mA cm^{-2} at 0.9 V vs RHE, and an half-wave potential of 0.86 V vs RHE. A deep accelerated potential cycling between 0 and 1.2 V vs RHE up to 5000 cycles demonstrated the remarkable stability of the Pt/Ti_3O_5-Mo catalyst, whose electrochemical surface area loss was accounted for only 11%, compared to the more than 81% loss of the commercial Pt/C reference

1. Introduction

Platinum (Pt), which is a highly efficient catalyst, is widely applied in proton exchange membrane fuel cells (PEMFCs) as cathodic side for the oxygen reduction reaction (ORR: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$). In the application of Pt catalysts, the supporting material is one of the most important factors when looking to enhance the electroactivity and stability of the catalyst. Carbon materials are extensively employed to support Pt catalysts in PEMFCs due to their excellent conductivity and high specific surface area. However, one of the main drawbacks of carbon supported catalysts is located at the cathode, which the electrode potential is relatively high in an acidic environment and carbon materials suffer corrosion under these conditions ($C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$, 0.207 V vs NHE at 25 °C). As a consequence, dissolution and agglomeration of Pt particles occur resulting in a decrease of electroactivity of the catalyst [1–4]. The Pt dissolution, which is an anodic reaction, causes a mixed potential at the cathode and subsequently the negative shifting of the ORR reversible potential. As a result, a huge decrease of the long-term stability of the catalyst performance occurs [1].

Among the candidates available for metal oxides supports, considerable attention has been paid to titanium suboxides (Ti_xO_{2x-1}, even known as Magnéli phases of titanium oxide) as a non-carbon material with high electronic conductivity, stability, and durability in acidic media. Substoichiometric Magnéli phases obtained from thermally treated TiO_2 in a reducing environment have electron conductivity similar to graphite thanks to oxygen vacancies in the crystalline lattice [5]. Moreover, chemically inert titanium suboxides materials are chosen because of economic reasons. These qualities make titanium suboxides an appropriate support for Pt-based catalyst utilization in PEMFC and DMFC [6–9], in particular for hydrogen fuel cell vehicles [5]. According to Walsh and Wills [10], the electrical conductivity of Ti_xO_{2x-1} depends on the suboxide 'x' value, but it is of the same order of magnitude as carbon. The electrical conductivity is greatest for x = 3 to 5, and it decreases at higher 'x' values. According to the literature, employing titanium suboxides instead of carbon as a support has the undoubted advantages of reducing the OH adsorption on Pt surface by lateral repulsion from the OH or O on the suboxide's support surface, and enhanced splitting of the O—O bond which is caused by the presence of oxygen vacancy sites on titanium suboxides support and preventing the dissolution of Pt from the surface of the

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support [11–16]. Moreover, the presence of Ti^{3+} defects and/or oxygen vacancies in titanium suboxides can act as a charge electron recombination centers, with a beneficial role in catalysis and photocatalysis, by reducing the electron-hole pair recombination rate [17,18], and favoring the *d*–*d* transition. Typically, titanium oxides containing Ti^{3+} show black or dark blue color because of the *d*−*d* transition on Ti^{3+} [19,20].

Among all possible titanium suboxides, trititanium pentoxide (Ti_3O_5) has been extensively investigated, and it exists in a variety of structural polymorphs, as a potential material for oxygen sensor and for photocatalytic properties [21–23]. Trititanium pentoxide is a metal-like compound with high conductive properties (conductivity higher than $600\ S\ cm^{-1}$) [10,24].

Since TiO_2 is a very stable compound, the formation of titanium suboxides in reducing environment requires long exposure at very high temperatures (>1200 °C). The presence of a metal, such as Mo, Co, Ni, Cu, [1,5,21] favors the evolution of TiO_2 into Magnéli phases at much lower temperatures. Moreover, according to the literature [25–27], Ti_xO_{2x-1}-M (with M = Co, Ni, Cu, Mo, Ru, Ir) as support plays a co-catalytic function together with Pt nanoparticles toward ORR. These supports not only solve the above-mentioned carbon-corrosion issues but also enhance the catalytic activity for ORR, due to strong metal–support interaction between the metal oxide and the Pt catalyst.

Pt/Ti_3O_5-Mo exhibits excellent properties as a catalyst due to the structural and electronic properties of Ti_3O_5-Mo [27–29]. In particular, Ti_3O_5-Mo has a high resistance to electrochemical corrosion which enhances the durability of the Pt catalyst. The positive effect due to the trititanium pentoxide is explained by considering the changes in Pt-*d* electronic properties and the geometric effect that produces the contraction of Pt–Pt bonding distance [30,31], leading to a favorable condition for electrochemical reactions. The activity enhancement of binary Pt/Ti_3O_5-Mo catalysts is attributed to the electronic donation of Ti_3O_5-Mo to Pt surface, which modifies the electronic structure of Pt surface atoms resulting in a weakened interaction between Pt and intermediates, freeing more active sites for O_2 adsorption [32]. This results in strong physical and chemical interaction with adsorbed gas species [33–35]. Finally, in our recent studies, we found out that the presence of Ti_3O_5 suboxide in a series of Pt/C-TiOx-C catalysts positively improves the performance toward the ORR, enhancing the stability under potential cycling [36].

In this study, a comparative evaluation of the structure, composition and electrochemical performance of the Pt/Ti_3O_5-Mo catalysts is discussed. A Pt layer was homogeneously deposited over the surface of the Ti_3O_5-Mo support. The resulting Pt/Ti_3O_5-Mo catalyst with intrinsic electrocatalytic activity and excellent stability in acidic media was applied toward the ORR. These efforts indicate that both Pt morphology and support structure can significantly enhance the catalytic activity and stability. The Pt/Ti_3O_5-Mo catalyst was characterized by X-ray diffraction (XRD), inductively coupled plasma atomic mass spectroscopy (ICP-MS), X-ray photoemission spectroscopy (XPS), transmission electron microscopy (TEM), field-emission scanning electron microscopy (FESEM), UV–vis measurements, and electrochemical long-term activity testing, including cyclic voltammetry (CV), linear sweep voltammetry (LSV), and accelerated potential cycling test (APCT).

2. Experimental part

2.1. Chemicals

Titanium (IV) oxide, anatase (TiO_2) 99.8 wt.%, chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$) ≥ 37.50% Pt basis, sodium borohydride ($NaBH_4$) 98 wt.%, potassium hydroxide (KOH) 85 wt.%, ammonium hydroxide (NH_4OH) 28.0% NH_3 basis, polyvinylpyrrolidone (PVP40: $(C_6H_9NO)_n$ average molar weight 40,000), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic® 123, average molar weight 5800), sulfuric acid (H_2SO_4) 95–98 wt.%, perchloric acid ($HClO_4$) 70 wt.%, Nafion® perfluorinated resin solution 5 wt.%, acetone (CH_3COCH_3) 99.5 wt.%, 2-propanol (C_3H_8O) 99.5 wt.%, and ammonium molybdate ($H_{24}Mo_7N_6O_{24}{\cdot}4H_2O$) were purchased from Sigma-Aldrich. A commercial platinum catalyst 20 wt.% on carbon black Vulcan XC-72R purchased from E-TEK was used for comparison tests. Nitrogen and oxygen gases were supplied in cylinders by SIAD with 99.999% purity. All aqueous solutions were prepared using ultrapure water obtained from a Millipore Milli-Q system with resistivity >18 mΩ cm.

2.2. Synthesis of titanium suboxide (Ti_3O_5-Mo)

The titanium suboxide Ti_3O_5 was prepared by doping commercial TiO_2 anatase with Mo ions. TiO_2 was dispersed in a solution of (70:30 vol.%) ultrapure water and ethanol respectively, followed by the addition of 2 wt.% Pluronic P123 surfactant. The obtained solution was stirred for 5 h at ambient temperature. Then 10 wt.% of Mo ($H_{24}Mo_7N_6O_{24}{\cdot}4H_2O$) was added to the solution. The pH of the solution was held constant at pH = 9 by adding NH_4OH. The mixed solution was continuously stirred at room temperature for other 5 h, evaporated at 120 °C, and finally dried at 80 °C for 12 h. The obtained powder was annealed at 850 °C (heating rate of $10\ °C\ min^{-1}$) for 8 h under a reducing atmosphere (H_2:N_2 10:90 vol.%).

2.3. Synthesis of Pt/Ti_3O_5-Mo

100 mg of Ti_3O_5-Mo support was dispersed in a solution of ultrapure deionized water and ethanol (30:10 mL) followed by adding 1 wt.% PVP surfactant. The solution was brought to pH 9–10 by adding NH_4OH and left stirring for 1 h. Then, 39.82 mg of $H_2PtCl_6{\cdot}6H_2O$ was dissolved in 10 mL of ultrapure deionized water and slowly reduced by adding 1 wt.% $NaBH_4$ at room temperature. This was then added to the support solution and left stirring for 5 h at an ambient temperature. The obtained solution was sonicated for 1 h and later left to stir for 5 h to allow for Pt adsorption. The resulting catalyst obtained after drying was heat-treated at 450 °C (heating rate of $5\ °C\ min^{-1}$) for 5 h under a reducing atmosphere (H_2:N_2 10:90 vol.%).

2.4. Chemical-physical characterization

The platinum-to-support weight percentage in the synthesized Pt/Ti_3O_5-Mo catalyst was determined by ICP-MS with a ThermoFisher Scientific ICAP-Q instrument. Prior to analysis, the samples were digested in hot concentrated HCl/HNO_3 3:1 mixture with some droplets of H_2SO_4.

The XRD patterns were recorded on a Panalytical X'Pert PRO diffractometer with a PIXcel detector, using Cu Kα radiation ($\lambda = 0.15418\ nm$), under the operating conditions of $2\theta = 20 - 90°$ and 2θ step size = 0.03, in order to examine the different polymorphs. The markers were located using the Philips X'Pert HighScore Software (ICDD database). The morphology of the support and the catalysts, and the characterization of the metals were observed by FESEM (JEOL-JSM-6700F instrument coupled with an energy dispersive X-ray spectroscopy (EDX) detector by OXFORD INCA). For the support, the STEM modality was employed to better enlighten the presence of Mo. The support was deposited on a copper grid with a graphitic carbon layer. TEM was carried out using a JEOL-2000 FXII microscope equipped with a LaB6 gun. 0.5 mg of samples was dispersed in 5 mL isopropyl alcohol and sonicated for