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Performance Improvement in Direct Methanol Fuel Cells by Using $CaTiO_{3-\delta}$ Additive at the Cathode

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Received: 8 November 2019; Accepted: 28 November 2019; Published: 2 December 2019

Abstract: A non-stoichiometric calcium titanate $CaTiO_{3-\delta}$ (CTO) was synthesized and used as oxygen reduction reaction co-catalyst (together with Pt/C) in direct methanol fuel cells (DMFCs). A membrane-electrode assembly (MEA), equipped with a composite cathode formulation (Pt/C:CTO1:1), was investigated in DMFC, using a 2 M methanol solution at the anode and oxygen at the cathode, and compared with an MEA equipped with a benchmark Pt/C cathode catalyst. It appears that the presence of the CTO additive promotes 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}, which is one of the highest values reported in the literature under similar operating conditions.

Keywords: $CaTiO_3$; oxygen reduction reaction; electrocatalysts; methanol tolerance; DMFC

1. Introduction

Direct methanol fuel cells (DMFCs) are electrochemical devices envisaged as convenient power sources for portable applications since they have high energy density, good energy conversion efficiency, and low environmental impact [1,2]. However, there are significant drawbacks to overcome in order to allow DMFCs commercialization; i.e., sluggish kinetics of methanol oxidation (MOR) and oxygen reduction (ORR) reactions, methanol cross-over through the polymer electrolyte membrane, and the high cost of the complete device [3–5]. In particular, the use of noble metal catalysts, both at the anode and cathode, significantly affects the cost of the DMFC [5]. Pt-based nanoparticles are the benchmark catalysts for MOR and ORR, but at the cathode compartment, they promote also methanol oxidation, resulting in mixed potential, which produces a decrease of the overall cell voltage [2].

Several approaches of the last decade were explored with the aim to reduce cost and improve ORR in the presence of permeated methanol [6–12]. Pt-alloys exhibit enhanced electrocatalytic activity for the ORR compared to Pt alone [13,14], due to both electronic factors (i.e., higher level of Pt d-band vacancy) and geometric effects (i.e., optimized Pt–Pt interatomic distance). In fact, a lattice contraction is realized, due to alloying, resulting in a more favorable Pt–Pt distance for the adsorption of O_2 [15,16]. Furthermore, alloying Pt with other transition metals can reduce the adsorption of alcohols on the cathode surface thanks to a dilution effect [17–22], since at least three adjacent Pt sites are needed for the dissociative adsorption of methanol [2,23].

An interesting approach to increase the performance of Pt catalyst is the addition of fillers that, thanks to their tunable surface properties, can act as Pt promoters. Several metal oxides have been investigated and studied as additives (or also as a support) for Pt-based catalysts such as SnO_2 [24], TiO_2 [25,26], ZrO_2 [27], IrO_2 [28] showing an enhancement in terms of activity and durability of the catalyst. Among these materials, TiO_2 has attracted a major interest because of its stability in acidic fuel cell environment, as well as the features of being inexpensive, safe (not toxic), and abundant in nature [29,30]. Nevertheless, TiO_2 material cannot be considered as a suitable catalyst support because unmodified and bulk titanium oxides present a low electrical conductivity [31].

According to the most recent literature, perovskite oxides are playing an important role as oxygen electrocatalysts especially in alkaline solutions, due to their favorable catalytic activity toward both the ORR and the oxygen evolution reaction (OER) [32,33]. Their success consists of their versatile and flexible structure (ABO_3) that can accommodate different dopant agents, such as transition metal ions (Fe, Ni, Co, Sr) on both the A and the B cations position, giving rise to a change in the band structure and to the formation of oxygen vacancies. These structural changes can modify the electrical properties of the material, influencing the catalytic activity [34]. The optimal ORR catalyst should possess moderate surface-oxygen interaction energy, allowing for the right balance between the adsorption and desorption of the reactants and the intermediates [35,36]. Consequently, a good promoter of ORR must to be able to facilitate the adsorption of oxygen and to establish a synergistic catalytic effect with the Pt catalyst.

Our idea, considering the above-mentioned requirements, has been to improve the properties of titanium-based oxides taking advantage from the perovskite structure. Here, we propose a non-stoichiometric calcium titanate $CaTiO_{3-\delta}$ (CTO) as an ORR co-catalyst for application in direct methanol fuel cells. This material, prepared by using a solvo-thermal method, has been recently investigated as a promoter of Pt/C catalysts for the ORR in rotating disk electrode (RDE), showing increased activity. The catalytic enhancement has been attributed to the presence of oxygen vacancies in the CTO structure, acting as available active sites for oxygen adsorption, facilitating a faster ORR [37]. In the present work, the most promising composite catalyst formulation (Pt/C:CTO 1:1) has been investigated at the cathode of a DMFC in order to increase the performance. Furthermore, an evaluation of the methanol tolerance characteristics of this composite cathode is herein presented.

2. Results

2.1. Physicochemical Characterization

A commercial 20% Pt/C was employed as a reference catalyst for the ORR. Figure 1 shows the XRD patterns of both the CTO powder, with an orthorhombic phase characterized by Pnma space group, and the Pt/C catalyst, with typical diffraction peaks of the face-centered cubic (fcc) structure of platinum. The average crystallite size of Pt and CTO was 2.1 ± 0.1 nm and 145 ± 5 nm, respectively. It appears that the Pt particles are very small, nanometric in size; furthermore, an amorphous halo is evident at about 30–35° 2θ. This commercial 20% Pt/C catalyst was selected due to the relatively high surface area as a consequence of these very small particles.

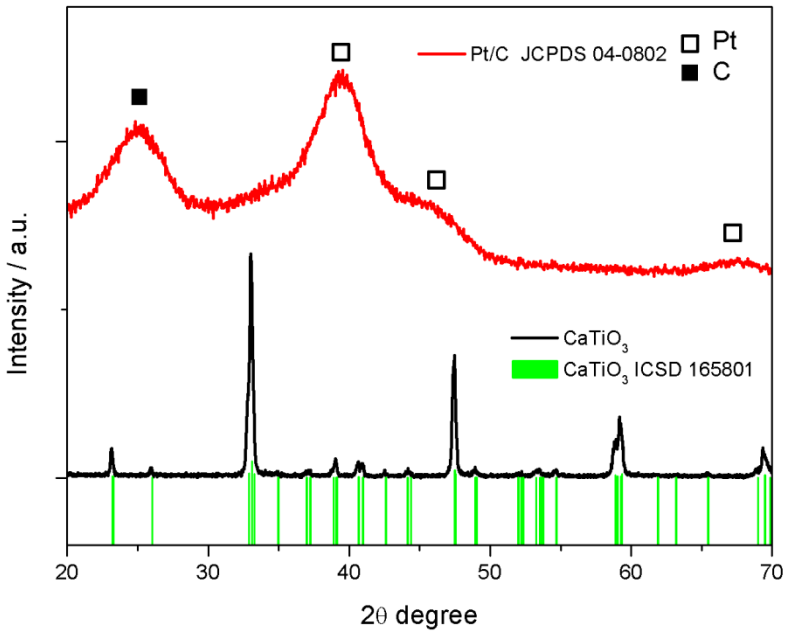

Figure 1. X-ray diffraction patterns of the synthesized $CaTiO_{3-\delta}$ powder and commercial 20% Pt/C catalyst.

The catalyst and the CTO additive were mixed together (in an ultrasonic bath) in a weight ratio of 1:1. SEM images of the mixture are reported in Figure 2. The images show a homogeneous distribution of the two compounds, with a prismatic, quasi-cubic shape of the CTO particles and the porous structure of the Pt/C catalyst (the typical morphology of carbon black can be observed in Figure 2a).

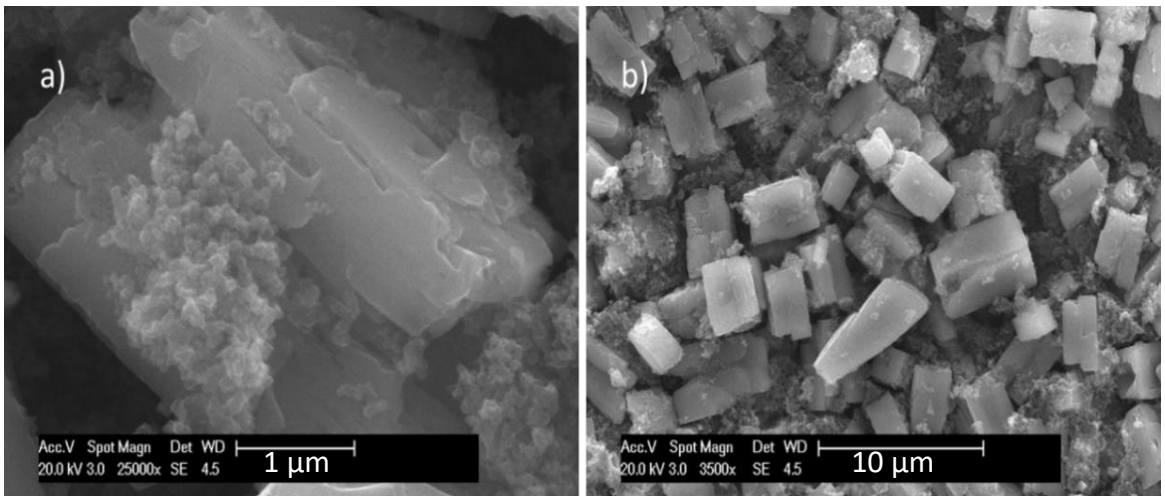

Figure 2. Scanning Electron Microscopy (SEM) images of the Pt/C-CTO (1:1) mixture at (**a**) high and (**b**) low magnification.

As reported in a previous paper [37], the composite material presents a higher electrochemical active surface area (ECSA) compared to the bare Pt/C (74 vs. 57 $m^2\ g^{-1}$), as determined by cyclic voltammetry (CV). This indicates that the mixing procedure does not create agglomeration of particles, but helps with increasing the interface and Pt utilization. This finding has been already reported for other transition metal oxides, added as promoters of Pt for different reactions (methanol or ethanol electro-oxidation, etc.) [38–42]. In this case, it appears that the presence of a sub-stoichiometric CTO increases the ECSA due to a local coordination of CTO particles with Pt [37].

2.2. DMFC Results

The Pt/C:CTO 1:1 composite material was investigated at the cathode of a DMFC, using a low Pt loading (0.5 mg cm^{-2}) at the electrode in order to assess the effect of the CTO addition on the electrochemical behavior. The same experiments were carried out on a membrane-electrode assembly (MEA) equipped with a bare Pt/C catalyst at the cathode, with the same Pt loading, for sake of comparison. The polarization and power density curves recorded for the two MEAs are reported in Figure 3 at three different temperatures (30, 60 and 90 °C), feeding the anode with a 2 M methanol solution.

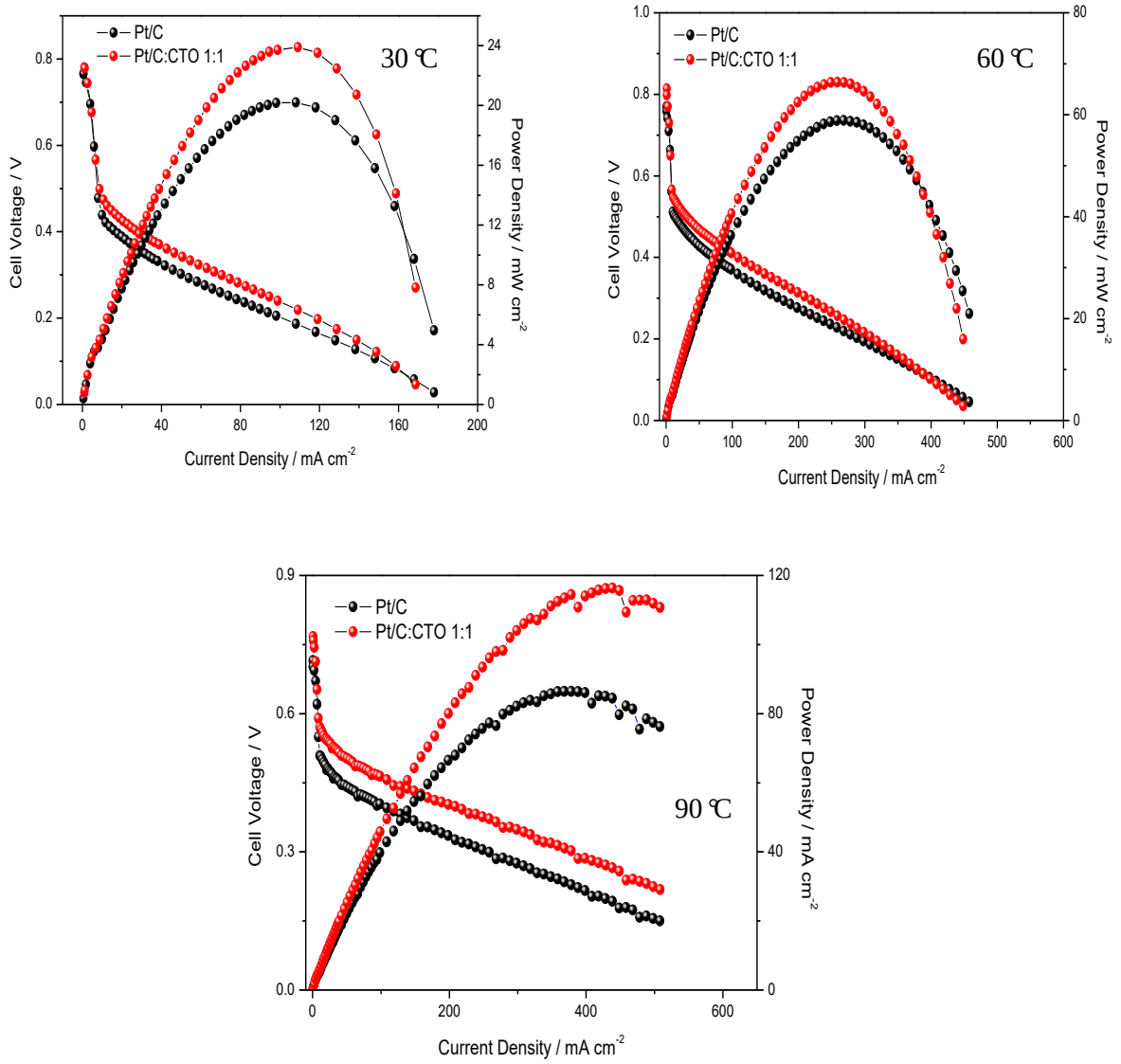

Figure 3. Comparison of DMFC polarization and power density curves for the MEAs equipped with the bare Pt/C (black) and the composite Pt/C:CTO (red) cathode catalysts at different temperatures (30, 60 and 90 °C).

From the polarization behavior at the different temperatures, it appears that the presence of the CTO additive promotes the oxygen reduction reaction, as already demonstrated by a previous work dealing with ex-situ RDE analysis [37]. In fact, by comparing the behavior at all investigated temperatures, the composite-electrode-based MEA showed a lower loss of potential in all the regions of the polarization curve, but, in particular, in the activation and ohmic regions. At higher current density, the diffusion of oxygen in a thicker cathode (due to the presence of CTO) for the composite

electrode likely produced a slight change in the slope of the polarization curve (visible at 30 and 60 °C, not at 90 °C since the polarization curve was interrupted before reaching the mass transfer constraints). The increase in power density, obtained with the CTO-based electrode, was around 15-20% at low temperature (30 and 60 °C), whereas it was more than 40% at higher temperature (90 °C). The maximum power density, close to 120 mW cm^{-2}, reached at 90 °C, is one of the highest values reported in the literature under similar operating conditions (2 M methanol at the anode, oxygen at the cathode under atmospheric pressure, 1.2 and 0.5 mg cm^{-2} Pt loading at the anode and cathode, respectively) [43]. The enhanced performance obtained with the CTO addition could be due not only to the improved kinetics of ORR, but also to a better methanol tolerance of the composite catalyst. In fact, higher open circuit voltage (OCV) values were recorded in the polarization curves at the different temperatures for the MEA based on CTO additive; this could be related to a lower effect of crossovered methanol on the cathode catalyst produced by the presence of CTO.

2.3. Methanol Tolerance Characteristics of the Composite Electrode: Ex-Situ Experiments

In order to investigate the methanol tolerance properties of the Pt/C:CTO mixture, ORR polarization curves in O_2-saturated perchloric acid solution, with and without methanol, were performed in a Rotating Disk Electrode (RDE) configuration (see Section 3, Materials and Methods). For sake of comparison, the same experiments were carried out on the bare Pt/C catalyst. The polarization behavior, without methanol and at an increasing concentration of methanol, is shown in Figure 4.

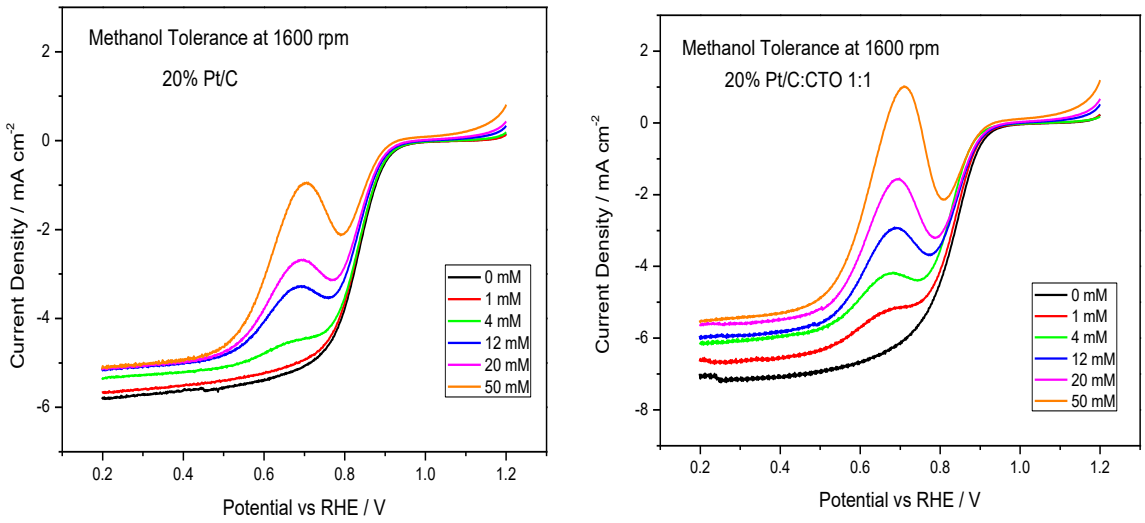

Figure 4. ORR linear sweep voltammetry (in RDE at 1600 rpm) without methanol and at increased concentrations of methanol for the 20% Pt/C (**left**) and the Pt/C:CTO 1:1 mixture (**right**).

Regarding the ORR activity without methanol, the Pt/C:CTO 1:1 catalyst showed the most positive onset potential (E_{ons}= 0.960 V), calculated at −0.1 mA cm^{-2}, and the largest limiting current density (j_d) value (7 mA cm^{-2}); whereas, the bare Pt/C exhibited an E_{ons} about 10 mV lower than the composite electro-catalyst with a j_d value of about 5.8 mA cm^{-2}. As clearly observed, the addition of methanol produces a slight shift of the ORR onset potential towards lower values, a reduction of the limiting current density and the presence of an oxidation peak (due to methanol). In particular, the intensity of the methanol oxidation peak is an indication of the catalytic activity of the catalyst towards that reaction. Since the intensity of the peak for the composite electrode is higher (the current density reached the region of the plot at positive values) than that observed for the bare Pt/C catalyst, it appears that the CTO presence favors the methanol oxidation reaction. This should be translated in a decreasing cathode voltage, due to a mixed potential caused by the simultaneous oxygen reduction and methanol oxidation reactions in the DMFC, larger than that observed for bare Pt/C. However, this was not observed in the fuel cell, since the OCV and the performance were higher for the MEA based

on the CTO additive. This could indicate that the promoting effect of the CTO is even larger than expected, since, as also confirmed by the RDE experiments in pure O_2, the performance obtained with the composite electrode was exceeding the one with bare Pt/C by 40% at high temperature (90 °C).

From the RDE results reported in Figure 4, it appears that CTO could promote methanol oxidation. To further confirm this feature, methanol oxidation reaction has been investigated in half-cell configuration (catalyst deposited on a glassy carbon working electrode, see Section 3), by comparing the response of CTO-based composite electrode and of Pt/C reference. The results are reported in Figure 5.

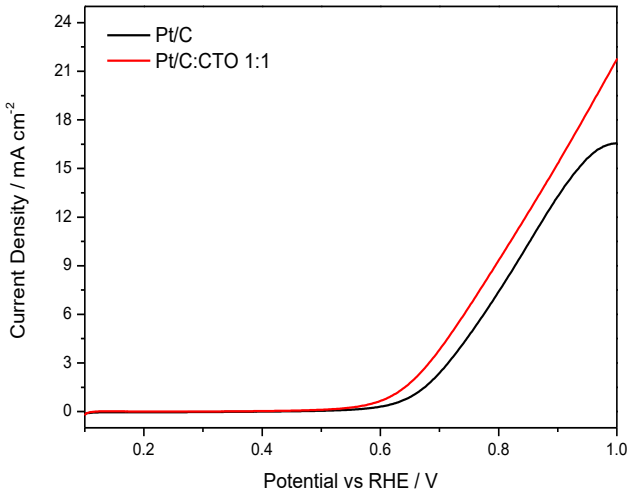

Figure 5. Linear sweep voltammetry for the methanol oxidation reaction in 0.1 M $HClO_4$ solution and 2 M methanol on Pt/C (black) and Pt/C:CTO (1:1) (red) mixture.

An increased current density and a negative shift of the onset potential are clearly observed for the composite Pt/C:CTO catalyst respect to bare Pt/C, confirming a promoting effect of CTO for the methanol oxidation reaction. This phenomenon may be explained through a bifunctional mechanism, in which dehydrogenation occurs on Pt sites and water can adsorb on CTO sites, acting like Ru in PtRu catalysts (benchmark material for methanol electro-oxidation) [2,44,45]. Accordingly, water displacement is favored on CTO sites (also due to the sub-stoichiometry), settling the good activity of some oxides to promote water discharge and adsorption of active oxygen species [2]. There is an analogy between the methanol oxidation and oxygen evolution processes; both require water adsorption and dissociation in oxygen species that, in the present case (methanol oxidation), give rise to surface reaction with adsorbed methanolic residues, producing CO_2 [2]. Similar results have been already reported by our group, where noble metal oxides (e.g., IrO_x and RuO_x) and valve metal oxides (e.g., SnO_x and VO_x) were added to Pt as promoters for methanol electro-oxidation reaction [46]. Other oxides with a perovskite structure were also found to be good catalysts for oxygen evolution reaction, in particular in alkaline media [47,48]. Thus, it appears that also the perovskite here proposed can have a beneficial influence on the methanol oxidation reaction, reducing the overpotential for water displacement and acting as co-catalyst. Furthermore, the increased ECSA reported for this composite electrode, compared to bare Pt/C, can also play a role in the increased activity. According to this evidence, it appears that the addition of CTO to the current benchmark anode catalyst (PtRu/C) in a DMFC could be of interest in the light of designing a multifunctional catalyst for methanol electro-oxidation. This aspect will be considered in a future work.

3. Materials and Methods

3.1. Synthesis of $CaTiO_{3-\delta}$

The synthesis of non-stoichiometric calcium titanate was carried out using a hydrothermal procedure followed by a calcination treatment, where Pluronic F127 was used as both structure-directing component and reducing agent to allow the formation of oxygen vacancies. This synthesis was carried out according to the details reported in our previous works [37,49].

3.2. Physical-Chemical Characterizations

The phase identification of the synthesized particles was performed using Rigaku D-Max Ultima+ X- ray diffractometer (XRD) (Tokyo, Japan) with a CuK_{α} radiation source at a potential of 40 kV and a current of 20 mA. The crystallites size was calculated using the Maud code.

The morphology analysis of the composite catalyst was conducted by scanning electron microscopy (SEM) using a FEI XL30 SFEG microscope (Hillsboro, Oregon, USA) operating at 25 kV.

3.3. Electrochemical Investigations

3.3.1. Rotating Disk Electrode (RDE) Screening

The electrochemical measurements were carried out using a Metrohm Autolab potentiostat/galvanostat (Utrecht, The Netherlands). Two different catalytic compositions were prepared and compared: Pt/C (E-TEK with 20 wt.% Pt content with respect to C), used as the reference, and Pt/C + CTO, with Pt:CTO 1:1 weight ratio.

A conventional three-electrode cell, formed by a mercury/mercury sulfate ($Hg|Hg_2SO_4$, saturated with K_2SO_4) reference electrode (RE), a high surface Pt wire counter electrode (CE) and a glassy carbon (GC) disk working electrode (WE), was used for the half cell electrochemical characterizations. The two catalytic inks (2 mg mL^{-1}) were prepared by adding the appropriate amount of catalyst powder in isopropyl alcohol and Nafion (30 wt.%), followed by ultrasounds treatment. The working electrode was coated with the prepared catalytic ink. Aliquots of this suspension were dropped onto the glassy carbon in order to obtain a final Pt loading, after the evaporation of the solvent, equal to 50 μg cm^{-2} for both the above-mentioned compositions. Prior to each deposition, the GC was polished with alumina slurry using an OP-felt polishing cloth.

Different methanol concentrations (0 mM, 1 mM, 4 mM, 12 mM, 20 mM, 50 mM) were studied in an oxygen saturated 0.1 M perchloric acid ($HClO_4$) solution, used as the electrolyte, at room temperature. Linear sweep voltammetry (LSV) was performed from 1.2 V to 0.2 V towards the reversible hydrogen electrode (RHE) with a scan rate of 5 mV s^{-1} at different rotations speeds (100, 200, 400, 1000, 1600, 2500 rpm). The activity toward methanol oxidation reaction (MOR) was investigated by LSV from 0.1 to 1 V vs. RHE with a scan rate of 5 mV s^{-1} in a 0.1 M $HClO_4$ in the presence of 2M CH_3OH solution.

3.3.2. Direct Methanol Fuel Cell (DMFC) Tests

The two membrane-electrode assemblies (MEAs) were realized by depositing the catalysts via doctor blade technique onto HT-ELAT and LT-ELAT (E-TEK) carbon cloths coated with gas diffusion layers at the anode and cathode, respectively. For the two MEAs, anode catalytic ink was prepared by sonicating 60% PtRu/C (Johnson Matthey, London, UK) and 33 wt.% Nafion ionomer (Ion Power, 5 wt.% solution) in 2-propanol/H_2O (3:1 v/v); the obtained slurry was deposited onto the carbonaceous substrate in order to achieve 1.2 ± 0.1 mg·cm^{-2} Pt loading. The membrane, employed for all the polarization measurements, was Nafion 117. The only experimental variable was related to the cathode catalysts. Pt/C (E-TEK) or Pt/C + CTO (Pt/C:CTO=1:1 weight ratio) was dispersed in 2-propanol/H_2O (3:1 v/v) and 33 wt.% Nafion ionomer (Ion Power, 5 wt.% solution) and then deposited onto LT-ELAT with the aim of achieving a low Pt amount (0.5 mg·cm^{-2}). The assembly was realized by hot pressing the membrane between the electrodes at 130 °C and 20 Kgf·cm^{-2} for 1.5 min.

A 5 cm^2 single cell, linked to a Fuel Cell Technologies Inc. test-station (Albuquerque, NM, USA), was employed for DMFC tests. Polarization measurements were recorded by feeding 2 M methanol solution at the anode, with a flow rate of 2 $mL \cdot min^{-1}$, and fully humidified oxygen at the cathode, with a flow rate of 100 $mL \cdot min^{-1}$. The performance of each MEA was measured in the temperature range 30–90 °C and atmospheric pressure.

4. Conclusions

A non-stoichiometric calcium titanate $CaTiO_{3-\delta}$ (CTO) was synthesized via an original template-driven hydrothermal procedure. The CTO powder was used as additive to Pt/C catalyst in a direct methanol fuel cell (DMFC) cathode. The cell tests revealed a positive effect of the perovskite for the composite electrode (Pt/C:CTO) especially at 90 °C and 2 M methanol, where a 40% increase of power density was obtained compared with the benchmark Pt/C, reaching a maximum power density close to 120 mW cm^{-2}. This was mainly attributed to the presence of oxygen vacancies in the CTO, but also to the increased ECSA caused by the mixing procedure.

The methanol tolerance characteristics of the Pt/C-CTO mixture were investigated in a rotating disk electrode (RDE) configuration, where it was found that the CTO presence favors the methanol oxidation reaction. This indicates that the promoting effect for the ORR of the CTO is even larger than expected, since there is a parasitic reaction of crossovered methanol oxidation that reduces the overall fuel cell performance. Accordingly, this composite catalyst is envisaged as also very promising for applications in the H_2-fed polymer electrolyte fuel cell cathode and direct methanol fuel cell anode.

Author Contributions: Conceptualization, M.A.N. and V.B.; methodology, A.S.A.; investigation, L.M. and C.L.V.; data curation, L.M. and C.L.V.; writing—original draft preparation, L.M. and V.B.; writing—review and editing, M.A.N. and V.B.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

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