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Short communication

Metal oxide nanoparticles synthesized by pulsed laser ablation for proton exchange membrane fuel cells

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ABSTRACT

We report on the development of a modified gas diffusion layer for fuel cells consisting of a simple or teflonized carbon cloth pulsed laser deposited with metal oxide nanostructures designed to operate both as co-catalyst, and oxidic support for other electrochemically active catalysts. We selected TiO_2, ZnO and Al_2O_3 doped (2 wt.%) ZnO which were uniformly distributed over the surface of gas diffusion layers in order to improve the catalytic activity, stability and lifetime, and reduce the production costs of proton exchange membrane fuel cells. We evidenced by scanning electron microscopy and energy dispersive spectroscopy that our depositions consisted of TiO_2 nanoparticles while in the case of ZnO and Al_2O_3 doped (2 wt.%) ZnO transparent quasi-continuous films were synthesized.

1. Introduction

A fuel cell is the device that directly converts the energy of a supplied gas, such as hydrogen, to electricity [1,2]. In case of proton exchange membrane fuel cells (PEMFCs), the base unit consists of a polymer electrolyte sandwiched by a pair of electrodes supported by gas diffusion layers (GDLs) [3–5].

Despite their simplicity, many difficulties have prevented the widespread usage of fuel cells, one of them being the low activity and high content of platinum electro-catalyst used for oxygen reduction. Till now, the best oxygen catalyst was considered Pt-based, but the drive to reduce metal loadings and costs and improve their efficiency requires the development of new materials and structures.

We herewith report the synthesis and characterisation of modified GDL containing metal oxide nanostructures as a possible solution to overcome the difficulties related to electro-catalysis and stability of electrodes. This type of structure was designed to function both as co-catalyst and oxidic support for other electrochemically active catalysts made of noble (Pt, Pd, Ru, etc.) or non-noble metals [6].

The oxide modified GDLs presented in this paper were synthesized using catalytically active components such as TiO_2, ZnO and Al_2O_3 doped (2 wt.%) ZnO uniformly distributed over the entire volume of GDL. We selected these compounds because they are expected to remain stable inside the oxidizing and acid media specific for PEM fuel cells. Moreover, the metal oxide-containing GDL structure is expected to prevent conductivity losses and allowing a good water and gases management [7–10].

Many different chemical and physical methods have been applied for the production of nanoparticles [11]. Among them, pulsed laser ablation (PLA) appeared to be one of the most promising alternatives. Nevertheless, the formation of nanoparticles during the PLA process is not yet completely understood. It is therefore important to continue the studies in order to elucidate the role of the various deposition parameters: incident laser fluence, ambient gas nature and pressure, number of applied pulses.

We applied PLA of pure targets for nanoparticles transfer to simple (SCC) or teflonized (TCC) carbon-based GDL. This method ensures an optimum stoichiometric transfer and uniform dispersion of the particles over the substrate surface and very good access of the reactants to the catalytically active sites.

2. Experimental details

The deposition of the metal oxide nanoparticles was performed inside a stainless steel vacuum chamber (Fig. 1). Before

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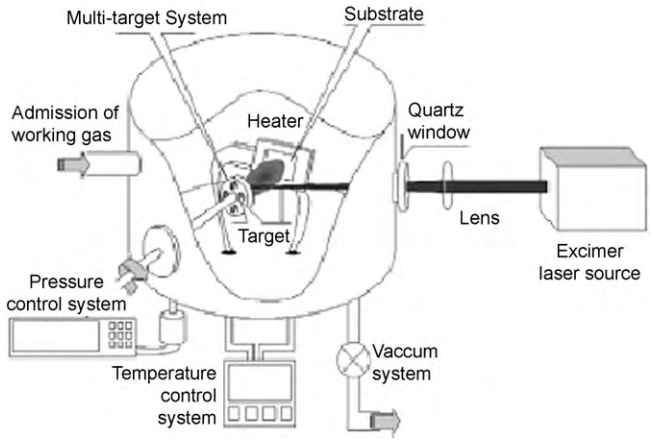

Fig. 1. PLD experimental set-up.

each deposition, the chamber was pumped down to a residual pressure of 10^{-4} Pa. UV laser pulses generated by a COMPEX-Pro 205 KrF* excimer laser source ($\lambda = 248$ nm, $\tau_{FWHM} \approx 25$ ns) were applied for the ablation of the TiO_2, ZnO and Al_2O_3 doped (2 wt.%) ZnO targets. The laser radiation was focused with an AR coated MgF_2 lens on target surface in order to melt, evaporate and ionize the ablated material [12]. The targets were simultaneously rotated and translated during experiments to avoid drilling. The ablation generates a transient, highly luminous plasma plume that expands rapidly away from the target surface. The ablation was performed in 1 Pa oxygen in order to confine the expulsed material and to compensate for the possible oxygen losses. The ablated material was collected on simple (SCC) or teflonized (TCC) carbon cloth positioned at 40 mm from the targets and kept at room temperature. The incident laser fluence was set at 1 or 5 J cm^{-2} for each type of target material. For the deposition of each structure, we applied 500 subsequent laser pulses.

The deposited structures were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) with a Carl Zeiss EVO microscope.

3. Results and discussion

3.1. TiO_2 nanoparticles

The SEM micrographs recorded for the TiO_2 structures deposited at two different laser fluence on teflonized carbon cloth are given in Fig. 2a and b. In the case of 5 J cm^{-2} laser fluence our studies confirmed the presence of TiO_2 nanoparticles. The deposited particles have sizes of tens to hundreds of nanometers. We observed (Fig. 2a) a uniform spatial distribution of the nanoparticles over the substrate surface. The density of TiO_2 nanoparticles was $\sim 5 \times 10^{-2}$ μm^{-2}. In the case of lower fluence (Fig. 2b), the number of nanoparticles was much smaller.

We noticed from the EDS analysis of the TiO_2/TCC structure obtained at 5 J cm^{-2} a uniform distribution of target elemental constituents (Ti—light blue and O—green) over the entire substrate surface (Fig. 3).

For TiO_2/SCC structure deposited at 5 and 1 J cm^{-2} respectively, the SEM images (Fig. 4a and b) show the presence of nanoparticles in low density. The EDS analysis (Fig. 5) confirmed the existence of target elemental constituents (Ti—blue and O—red) on the SCC substrate.

3.2. Al_2O_3:ZnO nanostructures

In Fig. 6a and b, there are presented the SEM micrographs recorded for Al_2O_3:ZnO/TCC nanostructures, obtained at 5 and 1 J cm^{-2}, respectively. The presence of few nanoparticles was visible after deposition at 5 J cm^{-2} laser fluence, accompanied by the formation of a shallow transparent film. For 1 J cm^{-2} laser fluence a rather quasi-continuous thin film was observed, without distinct nanoparticles.

The EDS analysis (Fig. 7) performed on Al_2O_3:ZnO/TCC at 5 J cm^{-2} put in evidence the presence of target elemental constituents (Al—light blue, Zn—pink, and O—green) with a uniform spatial distribution over the carbon cloth surface.

For Al_2O_3:ZnO/SCC nanostructures, we have obtained similar results as in the case of depositions on TCC.

3.3. ZnO nanostructures

Typical SEM images corresponding to ZnO/TCC nanostructures deposited at 5 and 1 J cm^{-2} are given in Fig. 8a and b. From these micrographs we observe the existence of a quasi-continuous layer without nanoparticles. The EDS analysis (Fig. 9) confirmed the presence and the spatial uniform distribution of the target elemental constituents over the TCC substrate.

Our studies revealed a different morphology of the three oxide nanostructures obtained under identical ablation conditions (incident fluence, laser spot, ambient gas nature and pressure). As the thermo-physical and optical parameters of the three oxides are rather close, this behavior is due in our opinion to the substance evolution after the impact on SCC or TCC. As known [13], in case of laser ablation at such fluence the material is expulsed in a plasma state and reaches the substrate in either vapor or liquid phase. It seems that TiO_2 is not wetting at all TCC, and but in a lower extent SCC. As a consequence, TiO_2 liquid droplets do not lay over surface, but freeze in the form of nanoparticles of different dimensions. Conversely, Al_2O_3:ZnO and especially ZnO wet rather well both TCC and

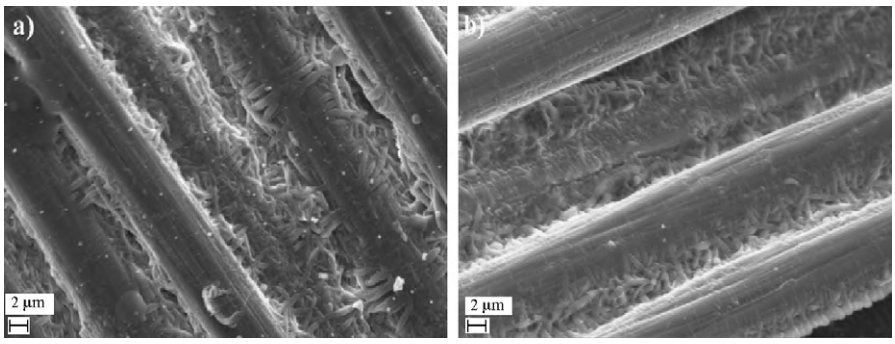

Fig. 2. Typical SEM micrographs of TiO_2 nanoparticles deposited on teflonized carbon cloth (TCC) substrate at a laser fluence of 5 (a) and 1 J cm^{-2}(b) respectively.

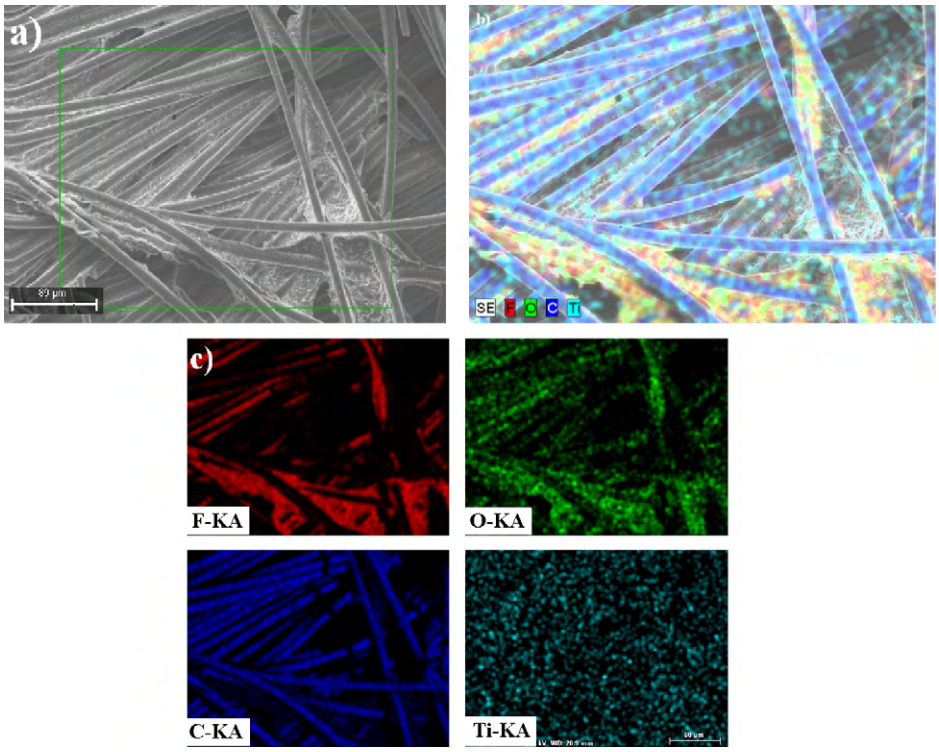

Fig. 3. (a) SEM micrograph, (b) elements map of the TiO_2, structure deposited on TCC at 5 J cm^{-2} laser fluence. (c) Detail from (b) with target elemental constituents: F, red; O, green; C, blue; Ti, light blue.

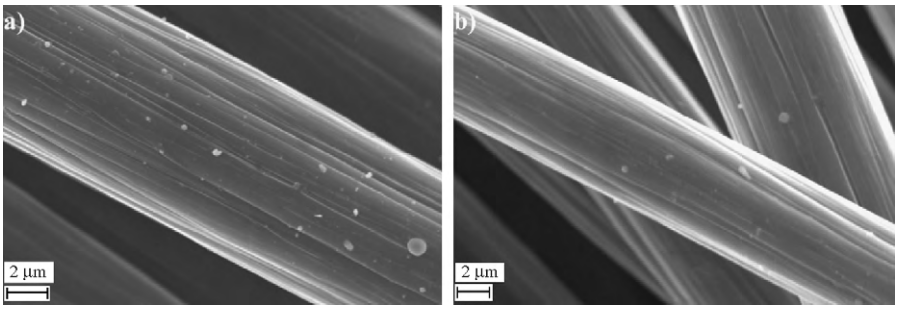

Fig. 4. Typical SEM micrographs of TiO_2, structures deposited on simple carbon cloth (SCC) substrate at a laser fluence of 5 (a) and 1 J cm^{-2} (b), respectively.

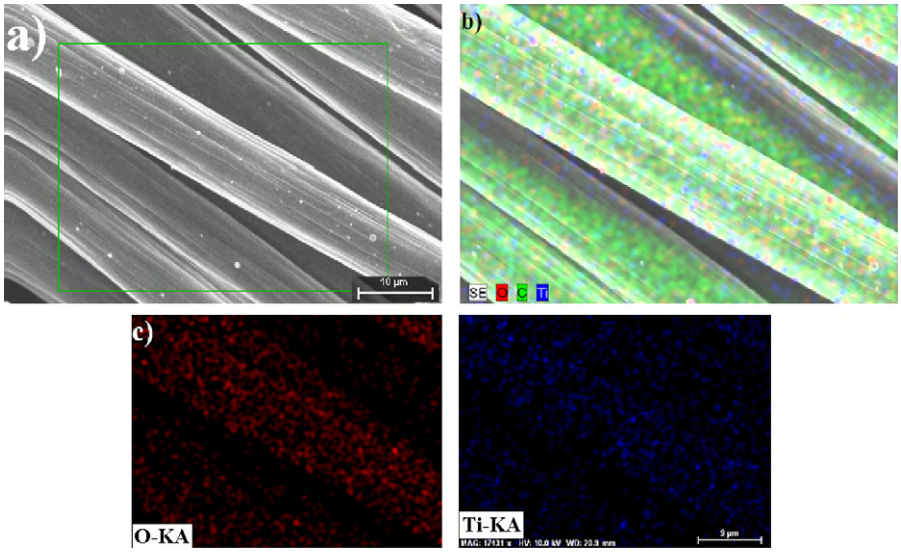

Fig. 5. (a) SEM micrograph, (b) elements map of the TiO_2, structure deposited on SCC at 5 J cm^{-2} laser fluence. (c) Detail from (b) with target elemental constituents: O, red; Ti, blue.

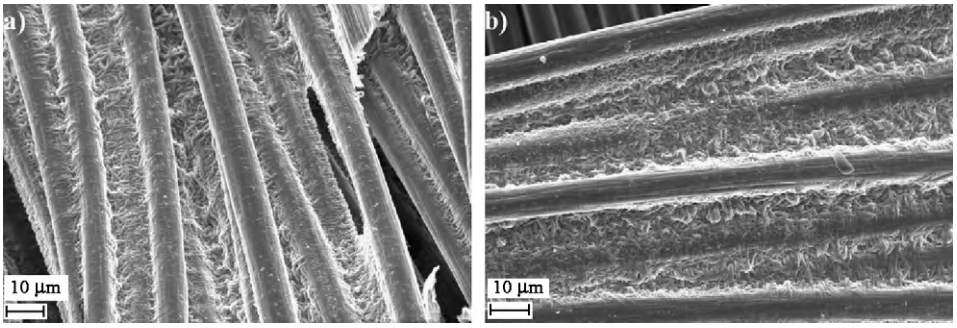

Fig. 6. Typical SEM micrographs of Al_2O_3:ZnO structures deposited on teflonized carbon cloth (TCC) substrate at a laser fluence of 5 (a) and 1 J cm^{-2} (b) respectively.

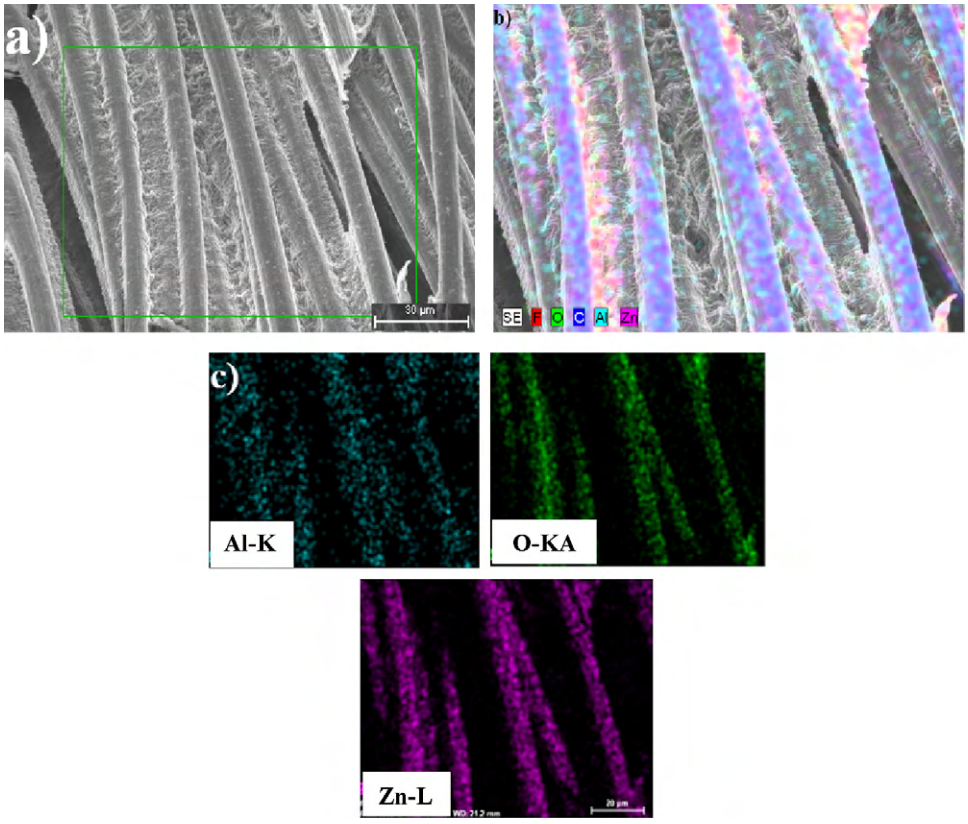

Fig. 7. (a) SEM micrograph, and (b) elements map of the Al_2O_3:ZnO structure deposited on TCC at 5 J cm^{-2} laser fluence. (c) Detail from (b) with target elemental constituents: Al, light blue; Zn, pink.

SCC, extend over surface and condense in the form of a very thin film.

The significance of these different evolutions is that one has to choose the appropriate oxide to deposit nanoparticles over a particular material of interest for PEMFCs, as, e.g. a metal mesh of nickel or steel. We found that in case of TCC and SCC, this oxide is TiO_2, but the studies have to be conducted similarly in case of any other GDL.

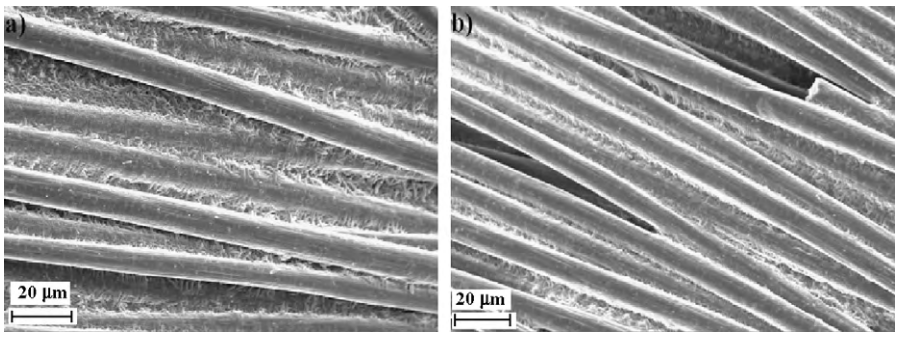

Fig. 8. Typical SEM micrographs of ZnO structures deposited on teflonized carbon cloth (TCC) substrate at a laser fluence of 5 (a) and 1 J cm^{-2} (b) respectively.

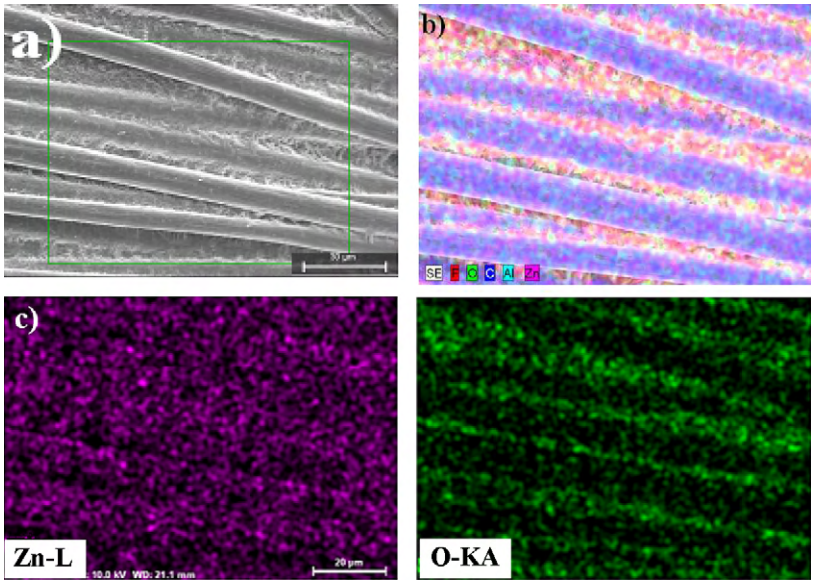

Fig. 9. (a) SEM micrograph, and (b) elements map of the ZnO structure deposited on TCC at 5 J cm^{-2} laser fluence. (c) Detail from (b) with target elemental constituents: O, green; Zn, pink.

4. Conclusions

The stoichiometric transfer of the material from TiO_2, Al_2O_3:ZnO, and ZnO targets on simple or teflonized carbon cloth substrates was obtained by optimizing the pulsed laser ablation regime. We synthesized by PLA TiO_2 nanoparticles with sizes within the range from tens to hundreds of nanometers on both TCC and SCC. We observed that the generation of well-defined nanoparticles with controlled size, shape and distribution can be tailored by the variation of the incident laser fluence. In case of Al_2O_3:ZnO and ZnO nanostructures, the formation of a transparent quasi-continuous film with a few or insignificant number of nanoparticles was evidenced. The uniform distribution of elements on deposition surface was demonstrated in all cases by EDS.

These features are compatible with the manufacture of PEMFCs. Cyclic voltammeter and electrochemical impedance spectroscopy measurements are in progress for the characterisation of the oxide modified GDL with respect of catalytic activity and electronic conductivity.

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