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Study of membrane electrode assemblies for PEMFC, with cathodes prepared by the electrospray method

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Abstract

The electrospray deposition of platinum supported on carbon (Pt/C) particles has been used for the preparation of electrodes for proton exchange membrane fuel cells (PEMFCs). The departing suspensions contain the Pt/C electrocatalyst together with an ionomer (Nafion®) and a solvent. Two types of solvent have been used, isopropanol and a mixture of butylacetate, ethanol and glycerol (BEG). The microscopic characterisation of electrosprayed films shows the electrospray deposited Pt/C films with a dendritic morphology. XPS analysis of the films reflects changes in the ionomer component after electrospray deposition. A decrease in the signal corresponding to backbone chain (CF_2) is observed on the films deposited with the low evaporation temperature solvent (isopropanol), indicating some disruption of ionomer chains during the electrospray process. With high evaporation temperature solvent (BEG), the disruption effect seems less acute. Membrane electrode assemblies were prepared with the electrosprayed electrodes as cathodes. Good general performance is encountered, comparable with standard commercial cathodes. Electrosprayed electrodes prepared from high evaporation temperature solvent (BEG) show a higher surface specific area. The internal resistance is something higher for MEAs with electrosprayed cathodes. The long term stability test shows a performance loss of about 10 $\mu V\,h^{-1}$ over 700 h continuous testing.

Keywords: Electrocatalyst; Electrospray deposition; Cathode; PEMFC

1. Introduction

One of the main objectives for future generations of polymer electrolyte fuel cells is cost reduction, which largely relies on a decrease of the platinum loading of the electrodes. This objective may be attained by different routes, like improved electrode preparation methods with higher control for platinum particle deposition, the search for high temperature tolerant membranes to promote electrocatalysis and hence reduce electrocatalyst requirements, or the search for new electrocatalyst materials other than platinum. Among novel electrode preparation methods, most interesting are those attaining thin films with high platinum dispersion and high surface area. In addition, the methods should be able to allocate platinum particles in a close proximity to the membrane surface to optimize the activity [1].

One interesting electrocatalyst deposition method is based on the electrospray effect. The electrospray effect consists of the transfer of a material (a liquid or suspension) to an aerosol phase (mist) under the action of an electric field [2]. From the aerosol phase, the material can be transferred to a substrate (electrospray deposition). Metal and compound nanoparticles have been deposited by electrospray and electrospray–pyrolysis with variable film morphology [3–6]. Localised deposition of organic and inorganic materials is possible with micrometric lateral resolution [7]. The electrospray effect is also applied for sample inlet in mass spectrometry [8] and for micro and nano-sized encapsulation [9].

Among the interesting properties of this technique, are the relatively simple experimental set up, which does not require special conditions in terms of temperature or vacuum, and the possibility to grow films with high uniformity and variable morphology. The electrostatic interaction between the charged particles and the surface substrate during electrospray deposition will prevent formation of agglomerates and favor the adhesion to the substrate. Surface morphology may be changed, depending on experimental parameters, such as substrate temperature,

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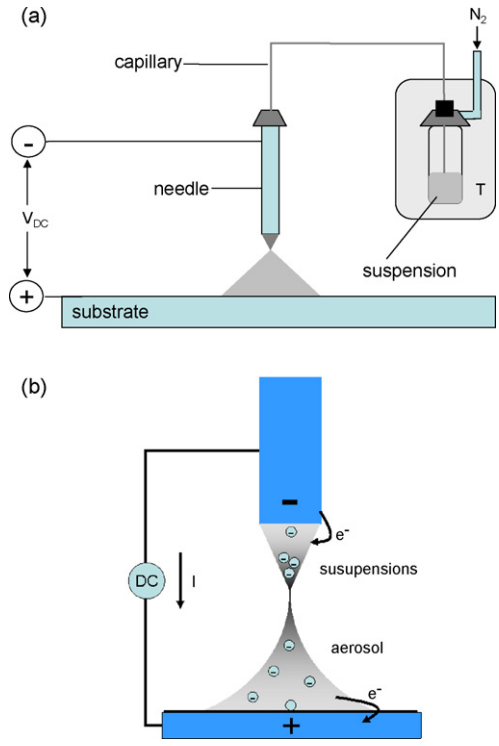

Fig. 1. (a) Scheme of the set up for electrospray deposition of Pt/C suspensions. (b) Detail of the electrospray process in the needle to substrate space.

liquid flow rate, dc voltage and tip-to-substrate distance, which control solvent evaporation and droplet size [6]. In addition, there is the possibility to use multiple electrospray jets [10,11] to increase the growth rates.

Electrospray deposition has already been used for the preparation of electrodes for PEMFC with good initial performance (1 A cm^{-2} at 700 mV, 80 °C and 300 kPa, using Nafion® 112 membrane and 0.36 mg cm^{-2} Pt loading), but significant mass transport losses [12]. In our laboratories, the electrospray deposition has been recently set up for the preparation of PEMFC electrodes [13], and studies about electrocatalysis for oxygen reduction have been performed on electrosprayed films with the rotating disk electrode [14].

Electrodes for PEMFC are usually prepared from a suspension containing the Pt/C catalyst together with a proton conductor (ionomer) in a solvent. The suspension is deposited onto the electrode substrate (carbon cloth, carbon paper) leaving, after solvent evaporation, a film ('active film') of the catalyst and ionomer, which exhibits both electronic and proton conductivity. Electrospray deposition of Pt/C films departs from the same type of suspension. During the electrospray process, the suspension is forced through a silica capillary to a metallic tip, where the liquid meniscus acquires a typical inverted cone shape (Fig. 1a). Here, a high concentration of ionised species (ions, molecules, particles) is created by electron transfer from the tip (Fig. 1b). The ionised droplets will reduce in size by evaporation of the solvent, and 'Coulomb explosion' occurs when the charge density on the drops overcomes surface tension forces, giving rise to an aerosol of very small and uniform ionised particles that are deposited and discharged on the substrate. The electrospray flux closes an electric circuit where a dc current flows, proportional to the deposition rate (Fig. 1b). For more details of the electrospray method we refer the reader to the specialised literature [3–11].

The electrospray process is very dependent on the presence of dissolved ions and surface charges on colloids and particles. Therefore properties like the dielectric constant of the solvent are of high importance. Other important properties are the density, viscosity and surface tension, which will control droplets size and flux rate.

In this work, electrodes for PEMFC have been prepared by the electrospray deposition method. For the preparation of starting suspensions, two liquids have been used, isopropanol and a mixture of butyl acetate, glycerol and ethanol (BEG). Membrane electrode assemblies (MEA) have been prepared using the electrosprayed electrodes as cathode, together with commercial electrodes as anode and Nafion 112 membrane. Results of the characterization in fuel cells are compared with those of MEAs prepared with commercial components.

2. Experimental

Suspensions of Pt/C powder (E-TEK, 20 wt%) were prepared using two different solvents, isopropanol and a mixture of butylacetate, ethanol and glycerol (BEG). Nafion® solution (Aldrich, 5% in aliphatic alcohols) was added to the suspension in 33 wt% of solids. Properties of the liquids alone and with the Nafion® solution added are given in Table 1. Viscosity (μ) was measured with a rotational viscosimeter (ST-DIGIT L); dielectric constant (ε) determined with a Liquid Dielectric Constant Meter (Bi-870); density (ρ) with a Gay-Lussac picnometer (Álamo); ionic conductivity (σ) with a conductivity cell (Beckman) and evaporation temperature (T_{evap}) from thermogravimetric analysis (Mettler Toledo).

The electrospray deposition was carried out on uncatalysed carbon cloth covered with gas diffusion layer (ELAT ETEK) over 29.2 cm^2 area, by imposing a dc voltage between 3300 and 4000 V (Bertran, Model 205B-10R), between a metallic needle

Table 1
Viscosity (μ), dielectric constant (ε), density (ρ), ionic conductivity (σ) and evaporation temperature (T_{evap}) of the solvent and mixtures used in this work for the preparation of Pt/C suspension, measured at 25 °C

Liquid medium/solvent	μ (cP)	ε	ρ (g cm^{-3})	σ (μS cm^{-1})	T_{evap} (°C)
BEG (45:50:5)	1.67	14.5	0.869	0.92	180
BEG + Nafion (33%)	**1.78**	**14.8**	**0.874**	**0.63**	–
Isopropanol	1.91	18.3	0.793	1.59	82.4
Isopropanol + Nafion (33%)	**2.04**	**22.4**	**0.804**	**1.07**	–

BEG, butylacetate/ethanol/glycerol (45/50/5).