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Formation of an integrated catalyst-coated membrane using electrohydrodynamic atomization Layer-by-Layer deposition for direct methanol fuel cells

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HIGHLIGHTS

- An integrated CCM was prepared using EHDA LbL deposition.
- The cathode of integrated CCM still presented compact feature after the life test.
- The 3 M methanol concentration gave the highest cell performance.
- The increase level of the cell performance decreased at higher temperature range.

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ABSTRACT

In this work, an integrated catalyst-coated membrane (CCM) is prepared by successively spray deposit Pt/C nano-suspension, Nafion solution and Pt–Ru/C nano-suspension on a cathode gas diffusion layer using electrohydrodynamic atomization (EHDA) Layer-by-Layer (LbL) deposition. Porous cathode and anode catalyst layers and dense Nafion membrane are deposited using the EHDA LbL deposition technique. It is also found that the EHDA LbL deposited CCM presents close packed structure. An 85 h life test shows that the EHDA LbL deposited cathode electrode side of the integrated CCM still presents well compact feature. Whereas, the delamination of the anode electrode side formed by direct pressing method is evident. The performance of the cell with different methanol concentrations is also examined. It is found that the 3 M methanol concentration gives the highest cell performance. Moreover, the polarization behaviour, methanol crossover and impedance response of the cell at different working temperatures are analysed. The cell performance demonstrates faster increase between 20 °C and 50 °C than between 50 °C and 70 °C. The methanol crossover test shows that the cell presents higher increase level of methanol crossover between 40 °C and 50 °C than other 10 °C temperature increase steps.

1. Introduction

Direct methanol fuel cells (DMFCs) have attracted considerable attention as an alternative power source for portable electronic devices such as cellular phones and laptops owing to their potential of high energy density, simple system configuration and low operating temperature [1–3]. In DMFC systems, the membrane electrode assembly (MEA) plays a key role, which consists of gas diffusion layers (GDLs), catalyst layers (CLs) and a polymer electrolyte membrane (PEM). MEA fabrication methods can be mainly categorized based on the substrate type used for the catalyst coating process, in which the catalyst could be coated either onto a gas diffusion layer (GDL-based MEA) or directly onto an electrolyte membrane (CCM-based MEA) [4,5]. It is reported that the MEA prepared by the CCM method provides better power density due to an extended catalyst/ionomer interface and improvement of catalyst utilization [6].

In the CCM method, the CLs are normally applied to both sides of the PEM by spraying [7], painting [8] and catalyst decaling [9]. The

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CLs and PEM are usually treated as individual elements during fabrication using the above methods. The delamination of CLs from PEM usually happens during repeated working process due to the low bonding energy between them [10], which can reduce the catalytic efficiency. In addition, the structure features, including particle size, particle arrangement and porosity of the CLs are difficult to control using the above fabrication methods due to the thick single layer coating and controlling difficulty of fabrication process [11], which consequently cannot adequately match the requirement of the CLs in DMFC.

Layer-by-Layer (LbL) deposition of multilayered ultra thin films in a simple way is considered as a promising and efficient method for the preparation of CCM [12]. A major advantage gained from LbL technique is the introduction of a large number of variables that can modify the CLs depending on the experimental conditions. Recently, this deposition method has attracted a number of researchers' attention [13–15]. Electrohydrodynamic atomization (EHDA) is a method capable of controlling deposition of nano-structures LbL via different working parameters, which makes it possible to provide a new way for forming CCM. EHDA is a physical process that makes use of electrical and mechanical forces to form a liquid jet and its further disintegration into droplets [16], which was first reported by Zeleny in 1914 [17]. The atomizer nozzle is usually made in the form of a metal capillary into which liquid or suspension can be pumped. Depending on the requirement of droplets/relics motion a plate, ring or point (positioned below the nozzle) is served as the ground electrode [18,19]. According to the geometry of the jet and droplet, the resulting atomization modes can be mainly classified as dripping, microdripping, spindle, multi-spindle, cone-jet and multi-jet [20]. Among these modes, the cone-jet mode, which is the steadiest mode of spraying, can regularize the break-up of the jet to generate fine and uniform droplets/relics ranging from micrometres to nanometres in size. Liquids are initially used in the process of EHDA, and the investigations on it are comprehensive [21,22]. The use of suspension and nano-suspension in EHDA is a more recent development [23,24]. The distinct advantages of this technique with the use of suspensions include its capability of forming fine and controllable deposition products and less risk of nozzle blockage during processing which is frequently observed with other droplet forming routes such as piezo-head drive ink-jet printing [25]. Moreover, droplets/relics formed by EHDA are charged, which can self-disperse in space, resulting in the absence of droplet coagulation [26]. This technique has shown great potential in recent years and has been introduced to produce nano-particles [27], deposit thin films [28] and direct writing micro-structures in bioengineering and chemical engineering [29,30].

In this work, an integrated CCM was prepared using the EHDA LbL deposition. The well dispersed and stable Pt/C nano-suspension, Nafion solution and Pt–Ru nano-suspension were prepared and atomize-deposited successively using the EHDA LbL deposition technique to form all components of the CCM. During the EHDA deposition the atomization characteristics of Pt/C and Pt–Ru/C nano-suspensions and Nafion solution and the deposited films of anode and cathode CLs and Nafion membrane were examined. The performance and life test of the integrated CCM were also studied.

2. Experimental

2.1. Catalyst suspensions and Nafion solution

The anode and cathode catalyst suspensions used to prepare the CLs using EHDA LbL deposition are Pt/C and Pt–Ru/C nano-suspensions. The Pt/C nano-suspension was prepared by first mixing 1.5 g of distilled water and 0.05 g of Pt/C catalyst powder (40 wt.%, Pt particle size ~4.5 nm, Johnson Matthey Plc, London, UK) by magnetic stirring for 10 min. Then 1.5 g of ethanol (99.7 wt.%, Tianjin Kermel Chemical Reagent Co., Ltd, Tianjin, China) and 0.1 g of Nafion solution (5 wt.%, DuPont, Wilmington, USA) was added and mixed under ultrasonic bath for 2 h. The Pt–Ru/C nano-suspension was prepared by first mixing 0.5 g of distilled water and 0.05 g of Pt–Ru/C catalyst powder (60 wt.%, Pt–Ru particle size ~6 nm, Johnson Matthey Plc, London, UK) by magnetic stirring for 10 min. Then 1 g of ethanol and 0.15 g of Nafion solution were added and mixed under ultrasonic bath for 2 h.

The addition of Nafion solution was to stabilize the suspensions and to increase the hydrophilic property of CLs, which can increase the transport ability of the electrochemical reaction products in fuel cells [31]. The use of ethanol as liquid carrier was due to its easy volatilization behaviour, which can simplify the drying process of the CLs. Spontaneous combustion can occur in the presence of concentrated, finely dispersed catalyst (Pt/C and Pt–Ru/C nano-particles) and organic solvents such as ethanol in atmosphere environment. The Pt/C and Pt–Ru/C nano-particles can lose their activity. Therefore, the distilled water was mixed with Pt/C or Pt–Ru/C catalyst prior to adding the ethanol.

The Nafion solution used for the preparation of PEM for DMFC using EHDA LbL deposition was prepared by the mixing of 5 wt.% Nafion solution (DuPont, Wilmington, USA) and appropriated methanol (99.5 wt.%, Tianjin Kermel Chemical Reagent Co., Ltd, Tianjin, China) under magnetic stirring for 0.5 h. Two Nafion solutions with different concentrations were used for the preparation of PEM using EHDA LbL deposition in this work in order to examine their effect on the feature of the Nafion membranes. The addition of methanol was to dilute the dense Nafion solution (5 wt.%) and to reduce the stress during the film formation process which can result in the crack of the Nafion membrane during the EHDA deposition process.

2.2. EHDA deposition of catalyst suspensions and Nafion solution

The EHDA deposition device is shown in Fig. 1, which comprises of an electrohydrodynamic needle coupled together with a computer controlled X–Y movement stage and a microscopic vision system. The X–Y movement stage consists of an X–Y stepper motor driven 2-axis system. The X and Y axes are mounted directly on one another and the top of the axis accommodates a 120 mm × 120 mm table for holding ground electrode and substrate. An end of travel limit sensor is fitted on each of the axes to trigger the controller when a respective carriage reaches a limit. The 2-axis system is computer-controlled using a programmable motion controller and Labview software. The needle (inner/outer diameter of 0.4/0.7 mm) was connected to a high voltage power supply (Teslaman Technology Co., Ltd, Dalian, China) and its inlet was connected to a syringe pump (Baoding Longer Precision Pump Co., Ltd., Baoding, China) using a silicone rubber tube through which suspensions/solution were pumped. The high voltage power supply was used to apply an electric field between the needle and the ground electrode, and the syringe pump was employed to provide the hydrodynamic force to push the suspensions/solution up to the outlet of the needle. An aluminium plate with a thickness of 6 mm, serving as the ground electrode, was placed directly on the table of the X–Y movement stage and connected to earth potential. The microscopic vision system with a magnification of range of 0.7–4.5× and focal length of 320 mm was used to allow observation of the characteristics of the suspensions/solution undergoing atomization.