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Reactive impinging-flow technique for polymer-electrolyte-fuel-cell electrode-defect detection

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HIGHLIGHTS

- Noninvasive technique defect detection in roll to roll electrodes identified.
- Modeling and experiments demonstrate optimal operating conditions for diagnostic.
- Infrared imaging with hydrogen excitation detects all GDE defects.

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ABSTRACT

Reactive impinging flow (RIF) is a novel quality-control method for defect detection (i.e., reduction in Pt catalyst loading) in gas-diffusion electrodes (GDEs) on weblines. The technique uses infrared thermography to detect temperature of a nonflammable (<4% H_2) reactive mixture of H_2/O_2 in N_2 impinging and reacting on a Pt catalytic surface. In this paper, different GDE size defects (with catalyst-loading reductions of 25, 50, and 100%) are detected at various webline speeds (3.048 and 9.144 m min^{-1}) and gas flowrates (32.5 or 50 standard L min^{-1}). Furthermore, a model is developed and validated for the technique, and it is subsequently used to optimize operating conditions and explore the applicability of the technique to a range of defects. The model suggests that increased detection can be achieved by recting more of the impinging H_2, which can be accomplished by placing blocking substrates on the top, bottom, or both of the GDE; placing a substrate on both results in a factor of four increase in the temperature differential, which is needed for smaller defect detection. Overall, the RIF technique is shown to be a promising route for in-line, high-speed, large-area detection of GDE defects on moving weblines.

1. Introduction

The development of the production of membrane-electrode-assembly (MEA) components using roll-to-roll processes [1–4] has resulted in overall polymer-electrolyte-fuel-cell (PEFC) cost reduction and production with improved throughput and repeatability [5,6]. For continuous processes, such as roll-to-roll, quality control during MEA component manufacturing has been identified as a critical issue [7,8]. Quality control for the moving two-dimensional functional surface, such as a gas-diffusion electrode (GDE), is challenging because the surface is in continuous motion and because of underlying heterogeneities across the GDE. A GDE sheet consists of a Pt-containing catalyst ink deposited on a porous carbon substrate (*i.e.* gas diffusion layer (GDL)). As the Pt electrocatalyst is a high-cost contributor to a PEFC stack, maximizing yield during production is of high importance. In addition, uniformity of catalyst-layer (CL) thickness is crucial for optimal PEFC cell performance [9–11]. Moreover, formation of cracks, voids and other mechanical defects in the GDE produced during a high throughput coating process can result in premature cell failure and component degradation [9,12–14].

Several rapid, nondestructive quality-control techniques are available for in-line defect detection for a GDE fabricated under a continuous process. Optical inspection of visible defects and measurements of coating thickness are used in the PEFC industry [15]. These techniques are limited in their applicability, as not all defects are visible, and offer limited probing depth due to light scattering [16]. More recently, X-ray Fluorescence (XRF) spectroscopy has

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been applied for measuring GDE Pt loading in-line [17,18]. However, XRF is a point measurement, and commercial systems are hindered by a slow acquisition time, thus inspecting a full 100% of GDE area is not feasible in real-time.

Infrared (IR) thermography with active excitation of the GDE material is a nondestructive evaluation tool that allows for complete, rapid, and noncontact defect detection [19–21]. We have demonstrated the feasibility of IR thermography coupled with direct-current (DC) electronic-excitation of catalyst-coated membranes [22] on an industrial-scale webline and reactive-flow-through (RFT) [23,24] excitation on stationary, enclosed GDEs. For RFT, a nonflammable (<4% H_2) reactive mixture of H_2/O_2 in N_2 is flowed through the GDE where the catalytic reaction on the Pt surface generates heat, creating a measurable thermal signature. A proof-of-concept of the extension of the RFT technique to an open-atmosphere environment, where the GDE is conveyed on a bench-top roller system, was previously reported and termed as reactive impinging flow (RIF) [25]. In this work, we report on the further development of the IR thermography technique coupled with RIF to detect defects in moving GDEs. In particular, we describe the transfer of the technique from a bench-top roller system to a research webline both experimentally and theoretically. For the latter, mathematical modeling is used to assess the optimal operation window for defect detection and explore the parameter space. Compared to the prior modeling work of RFT [10], the model developed in this work captures the physics of impinging flow onto the porous GDE on a moving webline. Moreover, this manuscript builds upon RIF technique demonstration [25] and explores optimal parametric space for webline velocity, gas flowrate, composition, and defect geometry for defect detectability. It also provides recommendations for improved defect detection using RIF technique.

The outline of the paper is as follows. First, the experimental setup of the research webline and fabricated GDEs are presented. Then, the model geometric domains, approximations, and physics are explained. Model calibration is performed against the thermal response of the pristine GDE on the stationary and moving weblines. Then, the detectability of defects is explored with the experiments and model parametric study. Lastly, methods to increase hydrogen utilization and improve defect detectability is discussed.

2. Experimental

The experimental work presented below was performed on an industrial-style roll-to-roll system built by Davis-Standard, which includes unwind and rewind stations to unroll; control speed, tension, and steering; and reroll sheet or roll material. Between the unwind and rewind stations, an experimental station is positioned, whereupon the RIF experimental components and infrared sensor were mounted. The line can handle web material up to 0.46 m width at speeds of 0.305–30.5 m min^{-1} and tensions of 87.6–876 N m^{-1}. An image of the webline, threaded-up with the GDE sheet fabricated for these experiments, is shown in Fig. 1.

The GDE sheet was fabricated in-house, such that it contained a variety of CL defects, by spraying Pt-containing catalyst ink onto a GDL substrate. The catalyst ink contained 49.5 wt% Pt/C catalyst from Tanaka (TKK TEC10E50E), 20 wt% Nafion® solution with 1100 EW from Ion Power, de-ionized water, and n-propanol. The Nafion®/carbon weight ratio of the ink was adjusted to 0.8. The ink was sprayed onto the substrate using a Sono-tek ExactaCoat spray system with a programmable 3D robotic gantry and a 25 kHz Sono-tek Accumist ultrasonic spray head. The nominal loading of the sprayed CL was 0.13 mg-Pt cm^{-2}. The substrate was an approximately 10 m long by 0.15 m wide sheet of GDL with a microporous layer (MPL) coating from AvCarb, LLC (formerly Ballard Material Products). Onto the midsection of the substrate, three successive 0.14 × 0.25 m sections of CL were sprayed, each having a different set of defects. Each section had five square defects, of sizes 0.0625, 0.13, 0.25, 0.5, and 1.0 cm^2. In one section, each defect had a 100% reduction in CL thickness, i.e. each defect was a bare spot. In another section, each defect had a 50% reduction in the CL thickness. And in the third section, each defect had a 25% reduction in the CL thickness. Thus, 15 defects were intentionally created of different size and thickness reduction. Fig. 1c shows a diagram of the sprayed section of the GDL sheet. Defects were created by masking the desired defect size during the spray process, as can be seen in Fig. 1d. The desired reduction in thickness was achieved by placing the mask on the surface for the appropriate fraction of the final spray passes, e.g. the last quarter of the passes for a 25% reduction of CL thickness. Fig. 1e shows an image of the defect sections of the GDE at 100% CL reduction. No figure is shown for the 25% CL reduction defect section, as the defects were not visible either by eye or optical imaging. The reader can appreciate that CL defects of <100% reduction consist of a discrete black area within a black surface, and thus are not easily detected by optical methods.

Fig. 1b provides a schematic diagram of the setup for the RIF webline experiments. Experiments were performed using a non-flammable gas mixture containing 2% H_2 and 1% O_2 in N_2. This gas mixture was chosen as a balance between maximizing the thermal response from the CL [23] and maintaining a safe, i.e. nonflammable, mixture. The gas mixture was delivered from a pressurized gas cylinder to the GDE surface through a gas knife using a bench-top MKS gas-flow-control system. A rectangular stainless steel plenum was used as the gas knife for these experiments. The knife had a linear array of laser drilled circular holes of 0.5 mm diameter with center-to-center spacing of 2 mm and a total cross-web length of 0.33 m. Reproducible positioning of the gas knife relative to the GDE surface was achieved by using micrometer screws with digital readouts that were integrated into the knife mounting assembly. Alignment of the gas knife relative to the cross-web direction was accomplished by shining light through the holes of the gas knife with a specially designed light source.

During all of the experiments, the GDE was oriented with the CL facing toward the IR camera and impinging gas flow. The operating conditions for the experiments were: (i) gas flowrate of 32.5 or 50 standard L min^{-1}, (ii) line speed of 3.048 or 9.144 m min^{-1}, (iii) substrate tension of 87.6 N m^{-1}, and (iv) 1 mm gas knife height from the GDE surface. The line speed used was intended to reflect current or near-term industry practice with regard to coating PEFC electrodes.

An IR camera (Jenoptik Vario-Cam HiRes) with a 640 by 480 pixel uncooled microbolometer detector was employed to capture the thermal signature of the GDE. The spectral range of the camera was 7.5–14 μm and its thermal resolution was 0.030 K. The viewing angle of the camera was orthogonal to the substrate. The camera was positioned downstream from the gas knife, relative to the motion of the substrate, at a height above the GDE surface such that the field of view included the gas knife and the excited GDE. IR data collected at a frame rate of 60 frames s^{-1} were captured with Thermography Suite (IRCameras, Inc.) software. Data consisted of time and temperature information for each pixel recorded with the IR detector. A uniform emissivity of 0.95 was used for the GDE. This value was determined using a comparative method [26] wherein the surface temperature of the GDE measured with the IR camera at a set temperature is compared to a material of known emissivity at the same temperature.