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# Thin film thermocouples for in situ membrane electrode assembly temperature measurements in a polybenzimidazole-based high temperature proton exchange membrane unit cell

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ABSTRACT

This paper presents Type-T thin film thermocouples (TFTCs) fabricated on Kapton (polyimide) substrate for measuring the internal temperature of PBI (polybenzimidazole)-based high temperature proton exchange membrane fuel cell (HT-PEMFC). Magnetron sputtering technique was employed to deposit a 2 μm thick layer of TFTCs on 75 μm thick Kapton foil. The Kapton foil was treated with in situ argon plasma etching to improve the adhesion between TFTCs and the Kapton substrate. The TFTCs were covered with a 7 μm liquid Kapton layer using spin coating technique to protect them from environmental degradation. This Kapton foil with deposited TFTCs was used as sealing inside a PBI (polybenzimidazole)-based single cell test rig, which enabled measurements of in situ temperature variations of the working fuel cell MEA. The performance of the TFTCs was promising with minimal interference to the operation of the fuel cell.



## 1. Introduction

The current low temperature PEMFC technology has attracted the scientific community to a great extent due to its high power density and non-polluting power source that produces little noise and have no moving parts. But it encounters major problems such as low CO tolerance and water management. To overcome these problems high temperature PEMFC technology has been adopted. The PBI (polybenzimidazole)-based high temperature PEMFC is well suited for applications especially for automotive industry, where liquid fuels are preferred as the fuel cell can be very well integrated with a reformer [1]. The PBI-based high temperature PEMFC has alleviated several technical problems that make it superior to low temperature PEMFC. The high operating temperature drastically increases the fuel cell CO tolerance [2,3], this simplifies the reformer based fuel cell system and thereby drastically reduces the cost. The PBI-based high temperature PEMFC does not need any humidification because the water content of the PBI membrane has less effect on the conductivity as compared to Nafion membrane [4], moreover water flooding problems are avoided as the cell operates at temperatures above the boiling point of water.

However, there are also certain challenges related to PBI-based high temperature PEMFCs which need to be resolved for efficient performance and long term durability of this fuel cell type. On one side high temperature (100–175 °C) enhances the $H_3PO_4$-doped PBI membrane proton conductivity and improves the electrode kinetics [5] but on the other side high temperature reduces the level of hydration of the membrane and accelerates the self-dehydration of $H_3PO_4$ above 130–140 °C [6]. The high temperature also assists the process of catalyst particles agglomeration and adversely degrades the performance of the fuel cell.

Thin film thermocouples are promising candidates among various types of temperature sensors for measuring temperature inside a working fuel cell because of their small size, fast response and flexibility in design and materials [7]. Several studies have been conducted in order to monitor temperature variations inside Nafion-based PEM fuel cell. A few of them have adopted thin film temperature sensors to measure the temperature inside Nafion-based PEM fuel cell. Lee et al. [8,9] utilized MEMS technology to fabricate micro-thin film temperature sensors based on resistance temperature detector (RTD) principle for the purpose of monitoring

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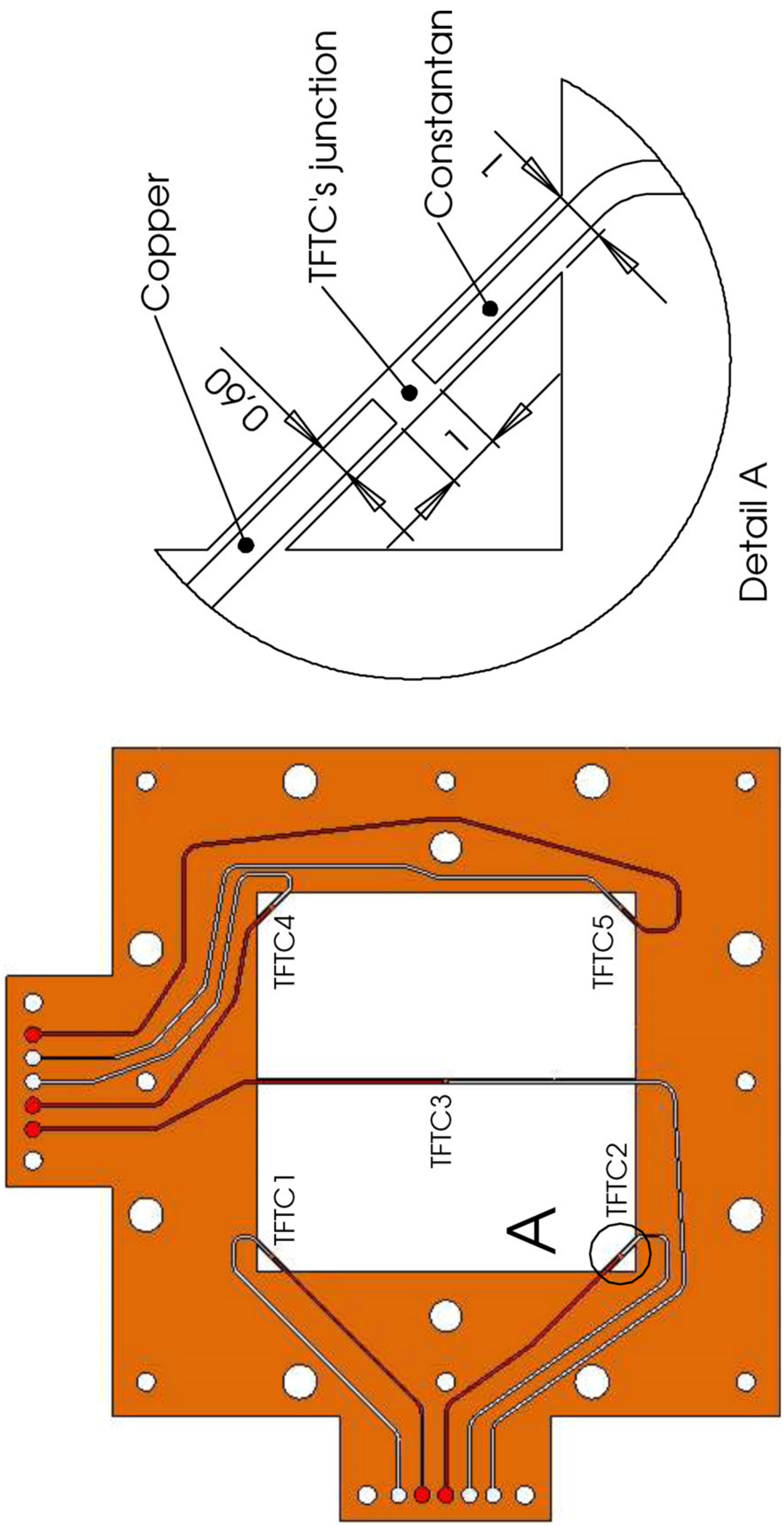


**Fig. 1.** TFTCs design layout.

in situ temperature on flow channel rib and in MEA of micro-fuel cells, respectively. He et al. [10] developed thin film gold thermistor using micro-fabrication techniques for in situ temperature measurement in a 5 $cm^2$ Nafion-based fuel cell during its operation. This thin film temperature sensor has a linear response in the 20–100 °C temperature range. All the previously mentioned studies have significantly worsened the performance of the fuel cell after embedding the temperature sensors inside the fuel cell.

The arguments within the literature for performing in situ temperature measurements of large size (~50 $cm^2$) PBI (polybenzimidazole)-based high temperature PEMFC is to understand different degradation mechanisms. This is indeed very scarce. Recently the author's group has conducted studies to provide insight of the in-plane and along the channel temperature variations of the MEA under various operating conditions in a PBI-based high temperature PEMFC unit cell [11]. In this investigation a total of 16 Type-T thermocouples were embedded on both the anode and cathode flow plates. The present work is the first study which focuses on the fabrication and utilization of Type-T (copper–constantan) TFTCs deposited via magnetron sputtering on Kapton foil. The Kapton foil serves two purposes, namely as a temperature resistant substrate for deposition of TFTCs as well as seal (gasket) of the fuel cell test rig. This TFTCs embedding technique offers some distinct advantages: (1) small size, (2) low cost, (3) robust and still relatively simple to be fabricated in connection with potential mass production, (4) functional in the working temperature range (110–200 °C) of HT-PEMFC, (5) temperature measurements as close as possible to MEA with minimum disturbance of the overall performance of the fuel cell.

## 2. Material selection and TFTCs design

### 2.1. Material selection

In this study Type-T (copper–constantan) TFTCs were selected due to their lowest temperature coefficient of resistance and the highest thermal emf [12]. The temperature measuring range for Type-T TFTCs is (−200 °C to 350 °C) [13] which was appropriate for the working temperature range (110–200 °C) of PBI-based HT-PEMFC.

Kapton foil was selected as a substrate for deposition of TFTCs because it is strong, tough and has a high glass transition temperature in the vicinity of 400 °C which reflects its high thermal stability. Kapton can be applied in conditions where temperature is as low as −269 °C and as high as 400 °C [14]. The selection of the substrate is crucial to the success of TFTCs embedding because it must provide good adhesion between substrate itself and TFTCs. The substrate also works as an isolating material, which is also very critical to prevent chemical reaction between TFTCs and the harsh fuel cell environments. The isolator for protecting the TFTCs should have excellent stability at the working temperature and the capability to form a high quality diffusion barrier against diffusing gases and phosphoric acid inside the fuel cell and a reasonable coefficient of thermal expansion to match that of the two metals used to form the TFTCs. In this work liquid Kapton, applied by spin coating, was selected as isolating layer as it is the same material as the substrate and due to its outstanding thermal and chemical stabilities and good thermal coefficient matching with thin film metal layers of TFTCs.

### 2.2. TFTCs design

The TFTCs were designed and then fabricated on a 75 μm thick Kapton foil. This Kapton foil was embedded in the fuel cell test rig as a seal in such a way that possible interference with the operation of the fuel cell was minimal. Fig. 1 illustrates the design layout of TFTCs, the red lines illustrate the copper material and the white lines illustrate constantan material. The overlapping area of copper and constantan alloy of 1 mm width constitutes the TFTC junction. The leg-width of the TFTC deposited on the Kapton foil was 600 μm.

## 3. TFTCs fabrication and microstructure evaluation

### 3.1. TFTCs fabrication on Kapton substrate

The procedure for fabrication of Type-T TFTCs involves three major steps: (1) deposition of TFTCs on Kapton foil via magnetron sputtering, (2) isolation of the surface of the TFTCs with liquid Kapton using spin coating technique, (3) cutting the deposited TFTCs on seal into the required size and cutting the hole for the MEA. Two special stainless steel shadow masks were prepared to cover the areas where deposition was undesired.

The sandwich assembly of shadow masks and Kapton foil was mounted on a fixture using magnets in a PVD chamber. One part of the shadow mask was used to deposit the copper portion first and the other part of the shadow mask was used to deposit the constantan portion of Type-T TFTCs, respectively as shown in Fig. 2, which illustrates the final seal with embedded TFTCs. Before depositing the TFTCs, the surface of the Kapton foil was prepared with plasma etching. This plasma etching was employed for 1 h using an argon gas flow rate of 40 ml per minute. The main purpose of this plasma etching on the Kapton substrate was to make the surface more reactive, and remove any remaining contaminations, for good adhesion between TFTCs and Kapton foil interface. The layers of copper and constantan alloy were deposited by magnetron sputtering at cathode power of 200 W per each cathode using 200 ml per minute argon flow rate. The pressure during the deposition process of Type-T TFTCs was around 450 mPa. The layers of 2 μm thick of copper and constantan films on Kapton foil were obtained in this way. The second major step was to protect the surface of the Type-T TFTCs against the harsh electrochemical environment inside the fuel cell using spin coating of liquid Kapton. The liquid Kapton was heated up to 120 °C and the samples were preheated in an oven at 120 °C. Before the spin coating process the contacts of the TFTCs were masked with Kapton tape to avoid deposition of liquid Kapton on the contacts. The liquid Kapton was applied to the sample in a smooth layer. Immediately after applying the liquid Kapton, the spin coating process was performed at 1800 rpm for 30 s. After the spin coating process, the samples were precured for half an hour at 120 °C. Curing was performed afterwards at 5 mbar vacuum with a flow of 50 slh $N_2$. During the curing process the temperature was

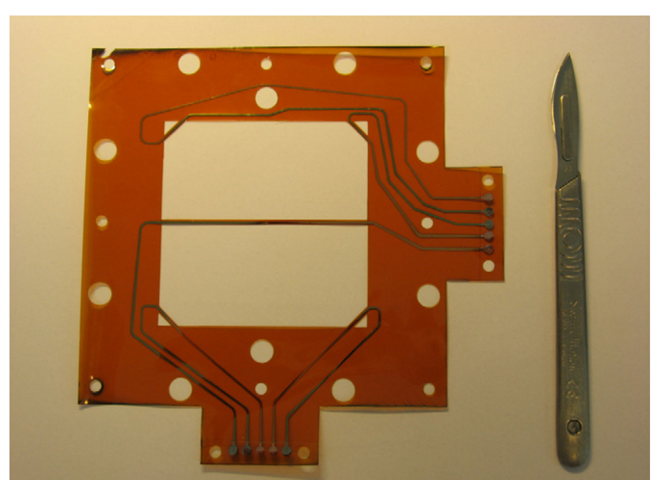

**Fig. 2.** TFTCs fabricated on Kapton seal via magnetron sputtering.

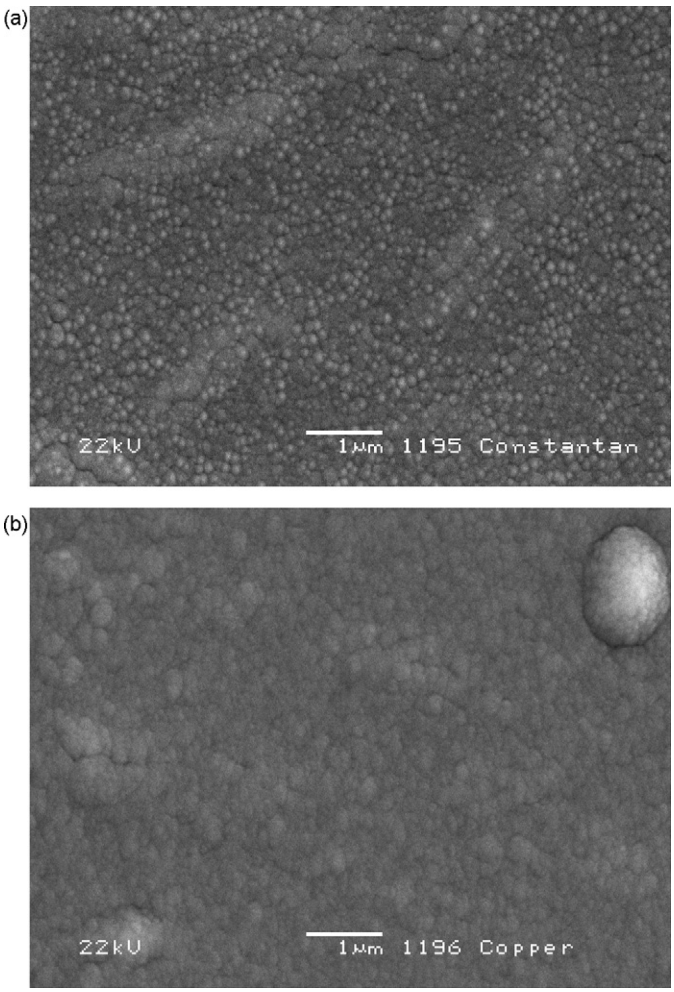


**Fig. 3.** (a) SEM image of constantan thin film and (b) SEM image of copper thin film.

first ramped up to 200 °C and fixed for 10 min, hereafter the temperature was ramped up to 320 °C and fixed for 10 min. Afterwards the samples were slowly cooled down to room temperature. The final thickness of the coating was achieved in the range of 5–8 μm.

### 3.2. Microstructure evaluation

The surface morphology of the TFTCs was investigated with SEM (JEOL Model JSM-5910). Fig. 3(a) and (b) shows SEM surface images of constantan and copper films, respectively. In these images constantan and copper film contain uniformly distributed clusters of their atoms which act as nuclei for further growth of the film.

The composition of the constantan film deposited by magnetron sputtering was also examined with EDS to ensure the right composition (55% Cu–45% Ni) for making Type-T TFTCs. The composition of constantan film was found to be around (63% Cu–37% Ni). The main reason for the observed difference in composition of the sputtered constantan film was due to a slight variation in composition during the life cycle of the constantan target (racetrack variations). These TFTCs were calibrated with respect to reference thermometer.

### 3.3. TFTCs calibration

The calibration of TFTCs was performed after the measurements on the PBI-based single cell test rig. The TFTCs were calibrated at the Temperature Reference Lab at Danish Technological Institute. The final TFTCs assembly was placed in a temperature reference

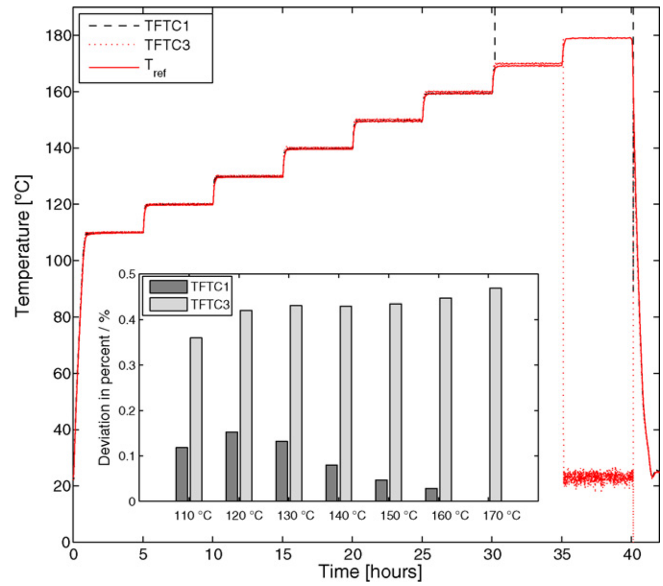


**Fig. 4.** Calibration curve of TFTCs showing TFTC temperature at seven different temperatures (110–170 °C, using a 10 °C interval) vs. reference temperature and deviation from reference in percent.

oven along with a PT1000 reference thermometer and calibrated at seven different temperatures (110–170 °C, using a 10 °C interval). The output from the temperature calibration can be seen in Fig. 4, which shows the calibration data for TFTC1 and TFTC3. The sensors show a good coherence to the reference sensor; especially TFTC1 only shows a maximum deviation of up to 0.15% from the reference sensor. It is however not a typical calibration curve for thermocouples, as they normally display linear deviation behaviour, with increasing deviation as the temperature rises. Moreover, the sensors show thermal instability, as the temperature is increased the sensors start to fail, TFTC1 fails when the temperature is increased to 165 °C and TFTC3 fails when the temperature is increased to 170 °C. This instability is believed to be caused by the connection interface to the sensors and not due to the actual deposited sensor, once the temperature is lowered both sensors start to work again. The reason for the latter and the non-linear deviation behaviour is at present unknown and will be the subject of future studies.

### 3.4. TFTCs embedding

The embedding of these TFTCs onto the membrane electrode assembly inside the high temperature proton exchange membrane fuel cell test rig was a challenging task as minimal interference to its normal operation was the goal. To ensure that the interface connections did not put too much stress on the seal sensors, Teflon frames were designed and fabricated. The Teflon frames therefore, support the TFTCs and interface the TFTCs with the data acquisition equipment. Fig. 5 illustrates the embedding of TFTCs on seal with Teflon support frame inside the single cell test rig.

## 4. Fuel cell test setup

Fig. 6 illustrates the schematic of the fuel cell test setup. The performance and durability of TFTCs on the Kapton seal were examined in this fuel cell test setup. From the TFTCs on the Kapton seal in the Teflon frame Type-T compensation wires were used to make the connections to the two cold junction boxes. Signals from the cold junction boxes were collected by a HP Datalogger (HP34970A) and converted into temperature readings by a Labview program. A sampling rate of 0.1 Hz was used to collect the

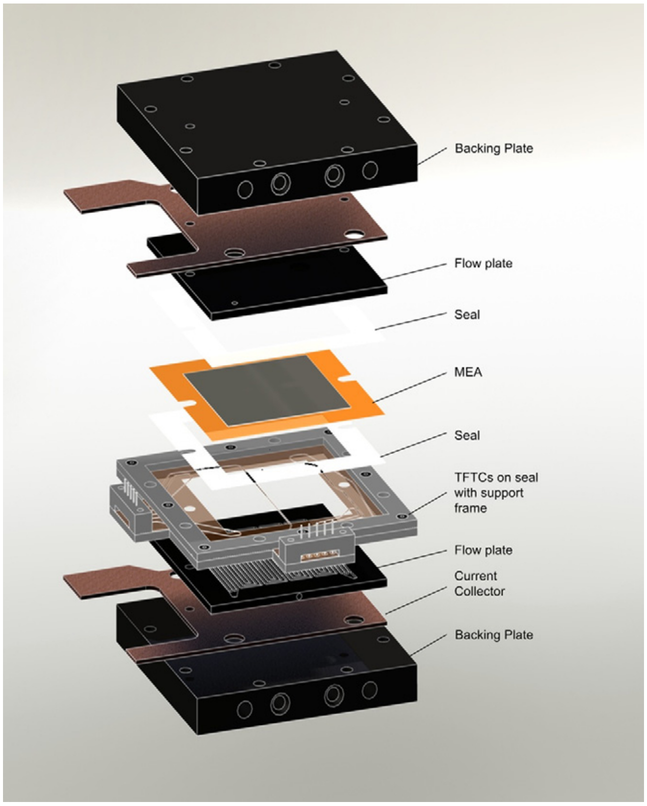


**Fig. 5.** Schematic view of embedding TFTCs seal assembly inside fuel cell test rig.

temperature data. The same Labview program controlled the flow of reactants through Burkert mass flow controllers (MFC 8711), the current drawn from the cell through a TDI dynaload (RBL488 50-150-800) and the heat applied to the cell through a Solid State Relay (SSR). A total fixed heat input of 2× 37 W was applied to the cell using the two heating elements on each side of the cell. The temperature of the cell was therefore floating and only governed by the heat from the cell reactions and to some extent by the ambient temperature. The MEA used in the test cell was the

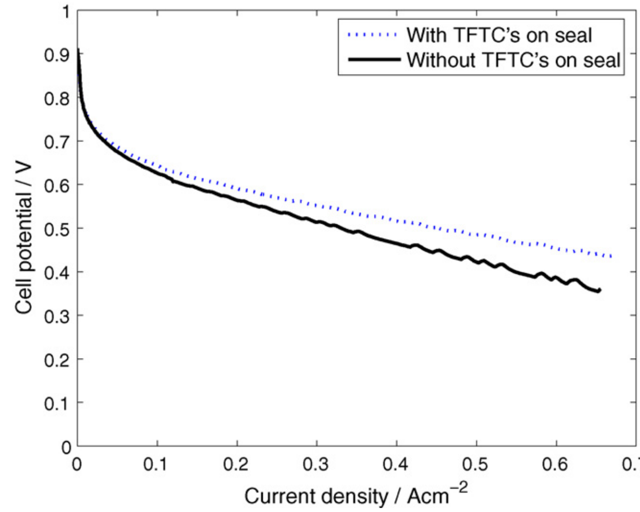


**Fig. 7.** Plot of cell performance with and without TFTCs at 160 °C and ambient pressure, $\lambda_{air} = 5$, $\lambda_{H_2} = 1.5$.

commercially available Celtic® P-1000 produced at BASF Fuel Cell GmbH (Frankfurt, Germany). Celtic® P membrane is polymer gel containing polybenzimidazole (PBI) and phosphoric acid. In commercially Celtic® P-1000 MEA the cathode contains a Vulcan XC 72 supported Pt-alloy with 0.75 mg cm$^{-2}$ and the anode contains a Vulcan XC 72 supported Pt catalyst with 1 mg cm$^{-2}$. Membrane thickness in the MEA is approximately 50–75 μm [15]. The unit test rig was also supplied by BASF.

## 5. Results and discussions

### *5.1. Influence of TFTCs on fuel cell performance*

The performance evaluation test was carried out in 45 cm$^2$ single fuel cell test rig using graphite flow plates. The cell was operated at 160 °C and ambient pressure using dry fuel (hydrogen) and air with stoichiometries of 1.5 and 5, respectively. The flow of the reactants was therefore proportional to the current drawn from the cell. When recording the performance curve, the cell was initially

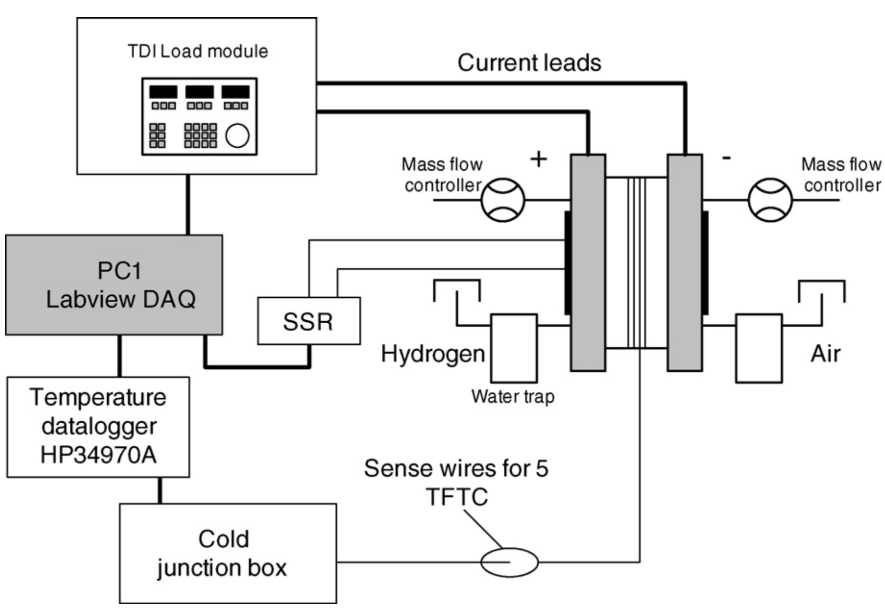


**Fig. 6.** Test setup for single cell temperature measurements.

heated up until a steady state cell potential and operating temperature was achieved, the current was hereafter increased linearly with 0.0333 A $s^{-1}$ (44 mA $cm^{-2}$ $min^{-1}$). First the performance curve was recorded without embedding TFTCs and in this case original seal thickness of the unit cell was 400 μm. Finally the performance of the fuel cell was analyzed using the same MEA by recording the performance curve after embedding the TFTCs seal assembly inside the fuel cell as shown in Fig. 7. The final thickness of the seal after embedding TFTCs seal assembly was 380 μm. Lee et al. [8,9] and He et al. [10] have reported severe degradation in performance after embedding temperature sensors inside a fuel cell. In the present study, performance was slightly improved probably due to lower thickness of the seal containing TFTCs. The lower thickness of the seal containing TFTCs resulted in a higher compression of the membrane electrode assembly (MEA) and more close contact between GDL and graphite flow plate. The close contact between GDL and graphite flow plate improved the contact area at the interface of GDL and graphite flow plate and reduced the contact resistance. A more detailed explanation can be found in Ref. [16]. It is, however, apparent that the TFTCs do not seem to degrade the performance of the fuel cell significantly. It is also important to notice that a performance enhancement is just as bad as performance degradation when evaluating the TFTCs disturbance.

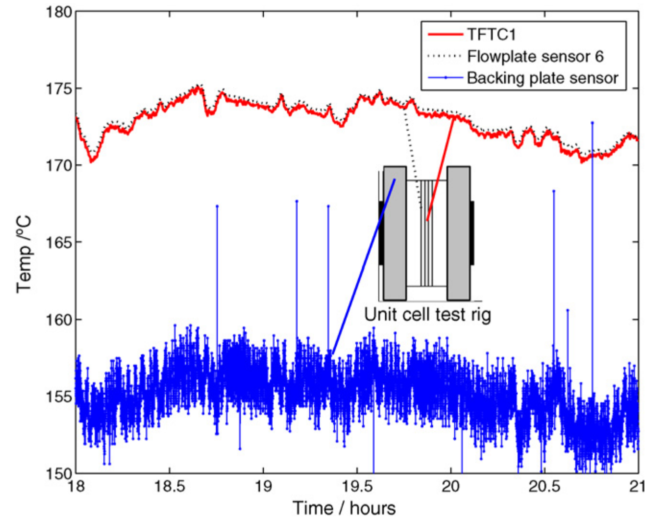


**Fig. 9.** Comparison of temperature measurements between TFTC, flow plate sensor and unit cell backing plate at a current density of 0.6 A $cm^{-2}$, ambient pressure, $\lambda_{air} = 5$, $\lambda_{H_2} = 1.5$.

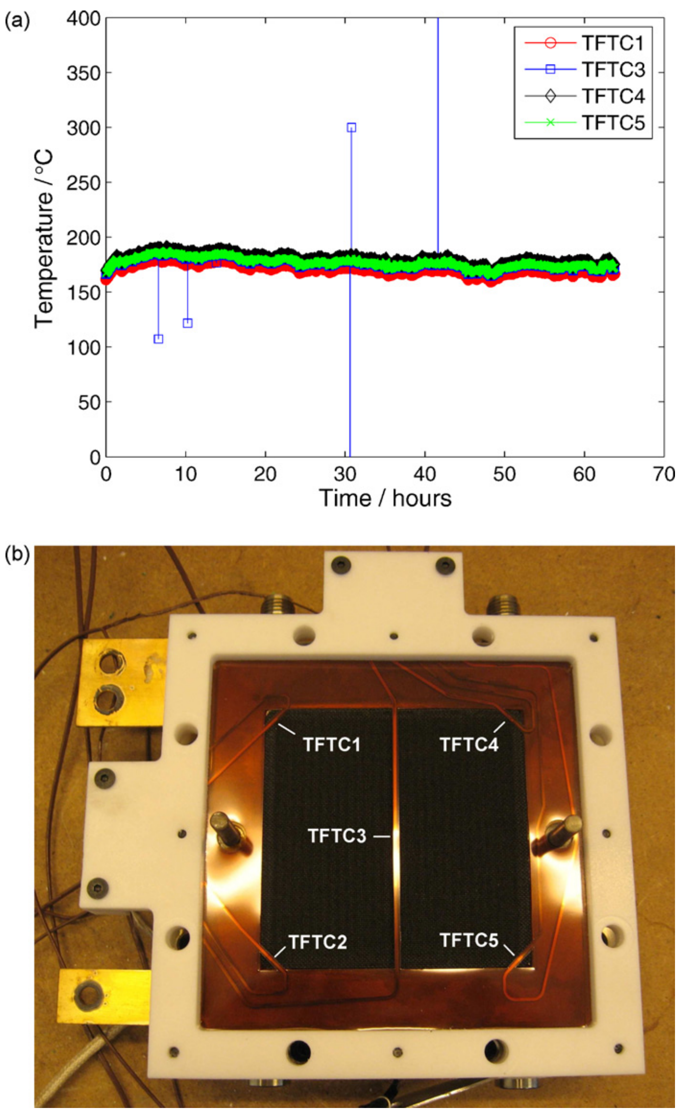


**Fig. 8.** (a) Performance evaluation test of TFTCs during 67 h operation at a current density of 0.6 A $cm^{-2}$, ambient pressure, $\lambda_{air} = 5$, $\lambda_{H_2} = 1.5$. (b) Top view of failed TFTC3 position located at the mid of the MEA.

### 5.2. Durability test

A test was performed for approximately 67 h at a current density of 0.6 A $cm^{-2}$ to evaluate the performance and stability of the TFTCs against the harsh electrochemical environment in a PBI-based proton exchange membrane fuel cell. The TFTCs output from this test is shown in Fig. 8(a). One of the five TFTCs embedded on the seal (TFTC2) was damaged during installation in the unit cell test rig. The performance of the remaining four TFTCs was very stable except one TFTC (TFTC3), which failed randomly. The same TFTC (TFTC3) was exposed to most of the area of the membrane electrode assembly as shown in Fig. 8(b), which inherently enhances the risk of failure.

### 5.3. Unit cell temperature variation

Naturally, there is a temperature variation among the different components of the unit cell test rig. The operating temperature is always an important parameter in any fuel cell test. However, as Fig. 9 illustrates, it is very important that the temperature should be measured in a representative position. Fig. 9 shows the temperature in the unit cell backing plate compared with graphite flow plate sensor in our previous study [11] and an in situ TFTC measurement. The temperature close to MEA, measured by TFTC followed exactly the same trend as the backing plate temperature changed. There is only minor difference between TFTC and flow plate sensor due to its placement very close to MEA. It is clear that the difference between TFTC and backing plate temperature is significant. If a single cell experiments are based on a backing plate temperature measurement, as shown in Fig. 9, it can lead to misleading conclusions as a 20 °C temperature difference in operating temperature can have a significant influence on the cell performance, e.g. the cell tolerance towards CO poisoning [2].

## 6. Conclusions

The present study investigates the fabrication; microstructural characterization and embedding of TFTCs for the harsh electrochemical environments as the inside of a high temperature PBI-based proton exchange membrane fuel cell. Based on thin film magnetron sputtering technology and the embedding method, a special TFTCs fabrication technique was developed to fabricate and embed TFTCs directly onto the membrane electrode assembly of the fuel cell. The TFTCs were embedded with minimal interference to the performance of the fuel cell. The performance of the TFTCs was satisfactory. This novel technique of TFTCs manufacturing opens new ways for in situ temperature measurements for fuel cells and other similar applications.

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