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Preparation and Characterization of Nafion/ Titanium Dioxide Nanocomposite Membranes for Proton Exchange Membrane Fuel Cells

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Abstract
In the present study, Nafion/Titanium dioxide (TiO_2) nanocomposite membranes for use in proton exchange membrane fuel cells (PEMFC) were investigated. Nafion/TiO_2 membranes were prepared using the recasting procedure. The composite membranes have been characterized by thermal analysis, XRD, SEM, proton conductivity measurements and single cell performance. Thermal analysis results showed that the composite membranes have good thermal properties. The introduction of the inorganic filler supplies the composite membrane with a good thermal resistance. The physico-chemical properties studied by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques have proved the uniform and homogeneous distribution of TiO_2 and the consequent enhancement of crystalline character of these membranes. The energy dispersive spectra (EDS) analysis indicated that the distribution of Ti element on the surface of the composite membrane was uniform. Performances of fabricated Membrane electrode assembly (MEA)'s measured via the PEMFC test station built at METU Fuel Cell Technology Laboratory. A single cell with a 5 cm^2 active area was used in the experiments. These results should be conducive to the preparation of membranes suitable for PEMFC. We believe that Nafion/TiO_2 nano composite membranes have good prospects for use in PEMFC.

1 Experimental

1.1 Membrane preparation

Nafion/TiO_2 composite membranes were prepared using the recasting method [1]. Nafion solution (15 wt.%) was evaporated at 60°C until a dry residue was obtained. The residual Nafion resin was redissolved in a desired amount of DMAc to form a solution containing 5 wt. % of Nafion. TiO_2 powder was added and dispersed in an ultrasonic bath. The resulting mixture was cast onto a Petri dish and the solvent was evaporated at 80°C. The membrane was removed from the Petri dish by wetting with de-ionized water. The membrane thickness around 80 µm was obtained from 10 wt. % TiO_2 loading. A recast Nafion membrane was also prepared with the same procedure for comparative study. All membranes were stored in deionized water before any test was performed. Before MEA preparation the membrane was treated by boiling in H_2SO_4 solution (0.5M) about one hour and washing in DI water for half an hour.

MEAs were prepared by spraying catalyst ink onto the gas diffusion layers (GDL 31 BC, SGL Carbon Germany) [2]. The catalyst ink was sprayed until the desired catalyst loading (0.4 mg

Pt/cm2 for both anode and cathode sides) was achieved. After spraying the catalyst ink onto the GDL's, MEA was prepared by pressing these GDL's onto the treated membrane at 130^0C, 688 N cm-2 for 3 min. Performances of fabricated MEA's were measured via the PEMFC test station built at METU Fuel Cell Technology Laboratory. A single cell PEMFC (Electrochem FC05-01SP-REF) with a 5 cm^2 active area was used in the experiments.

1.2 Characterization

The composite membranes have been characterized by thermogravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD) and single cell performance. The energy dispersive spectra (EDS) analysis indicated that the distribution of Ti element on the surface of the composite membrane was uniform. Performances of fabricated MEA's were measured via the PEMFC test station built at METU Fuel Cell Technology Laboratory. The membranes were tested in a single cell with a 5 cm^2 active area operating at 70 °C to 120°C.

2 Results

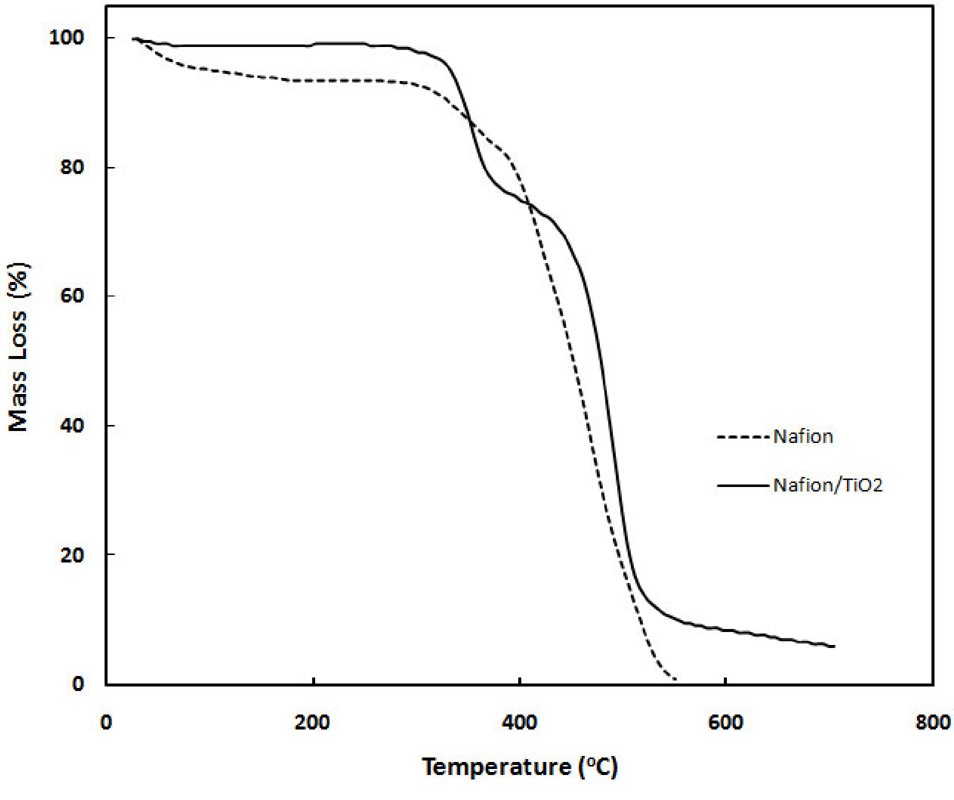

Figure1: TGA curve of Nafion and Nafion/TiO_2.

Thermal analysis results showed that the composite membranes have good thermal properties. The introduction of the TiO_2 supplies the composite membrane with a good thermal resistance (Figure 1). There is three derivative weight loss peaks for Nafion around 50^oC – 200^oC, 200^oC –400^oC, and 400^oC –550^oC. Initial weight loss is due to residual water. The next peak is attributed to the decomposition of the -SO_3H groups and the final peak is assigned to the degradation of the polymer main chain. Nafion/TiO_2 composite membranes have good thermal stability. The results indicates that addition of inorganic TiO_2 do not change the thermal stability of Nafion. The decrease of the degradation temperature observed in the Nafion/TiO_2 composites has been associated with a catalytic effect of titania and chemical interaction between the acid groups in Nafion and the surface of the TiO_2 particles [3,4].

The physico-chemical properties studied by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques have proved the uniform and homogeneous distribution of TiO_2 and the consequent enhancement of crystalline character of these membranes.

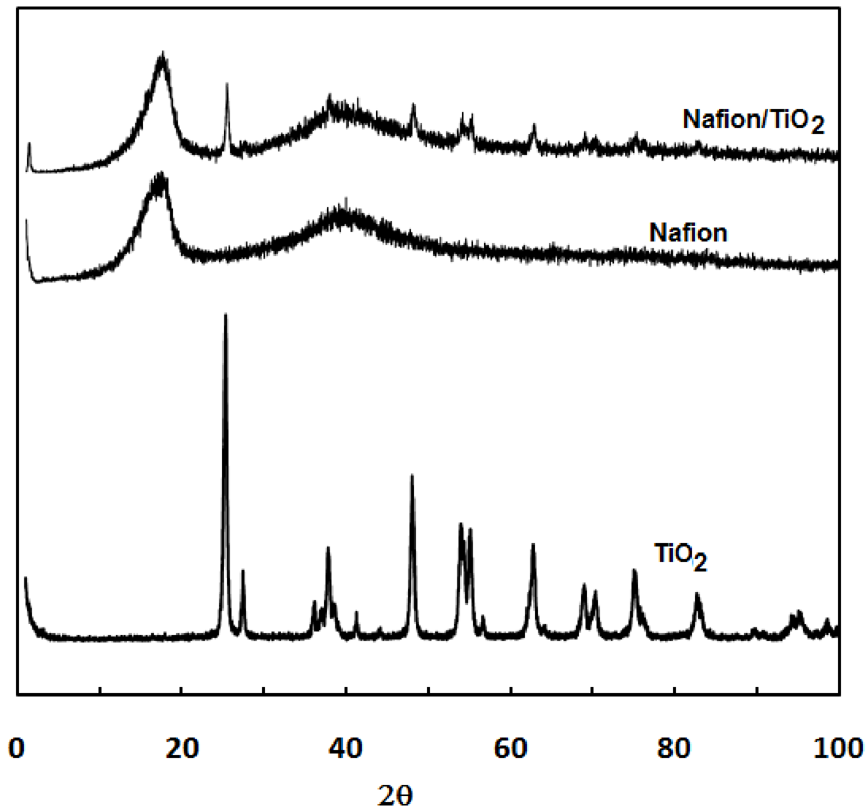

Figure 2: XRD patterns of Nafion, TiO_2 and Nafion/TiO_2.

As seen from Figure 2. the crystallinity of the composite membrane increases when 10 wt% TiO_2 is incorporated into membrane. The increase in crystallinity suggests that the interface adhesion is strong between inorganic additives and organic polymer structure due to the structural modification [5,6].

SEM analysis has proved the uniform and homogeneous distribution of TiO_2 (Figure 3). The energy dispersive spectra (EDS) analysis indicated that the distribution of Ti element on the surface of the composite membrane was uniform.

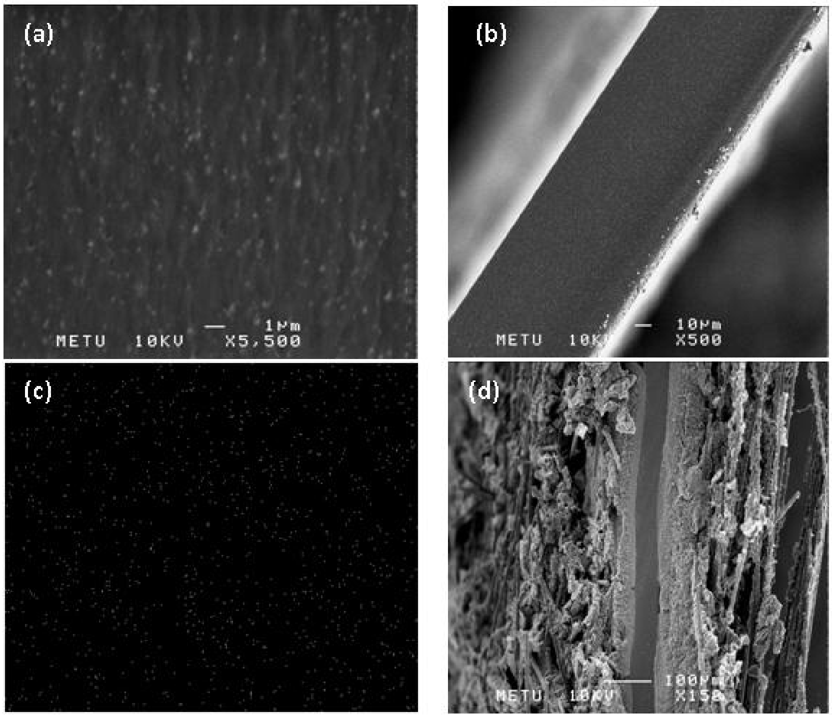

Figure 3: SEM images of a) Nafion/TiO_2, b) cross section of Nafion/TiO_2, c)Ti distribution by EDS, d) cross section of MEA prepared by Nafion/TiO_2.

Figure 4 and 5 illustrate the polarization curves obtained at different cell temperatures for the membrane electrode assemblies (MEAs) prepared with Nafion and Nafion/TiO_2 composite membrane. The maximum power reached for the cell constructed with Nafion/TiO_2 composite membranes is 0.266, 0.218 and 0.18 W/cm^2 for the cell operating temperatures of 80, 85 and 90^{o}C, respectively. The maximum power density measured for the cell constructed with Nafion/TiO_2 composite membrane is more than the cell constructed with Nafion membrane. Single fuel cell tests performed at different operating temperatures indicated that Nafion/TiO_2 composite membrane is more stable and also performed better than Nafion membranes.

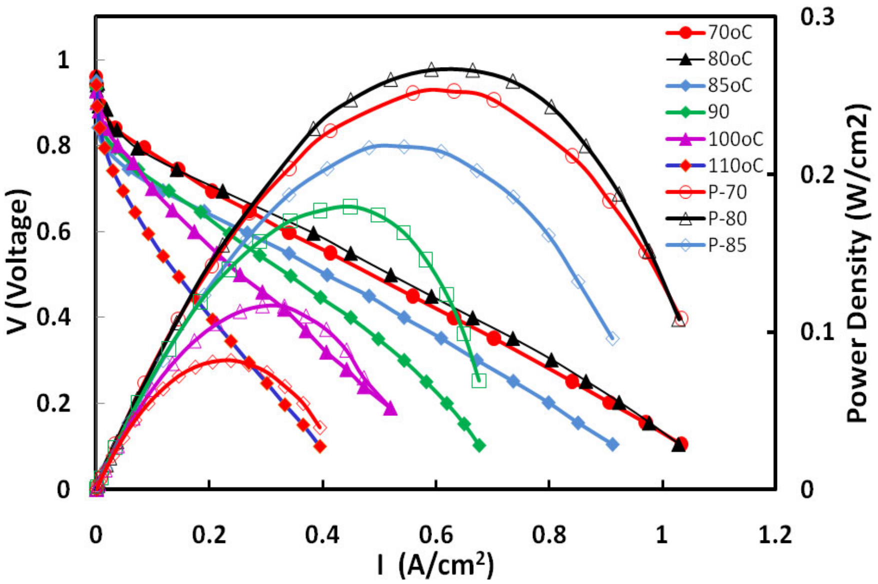

Figure 4: VI curve of Nafion/TiO_2 composite membranes at different temperature.

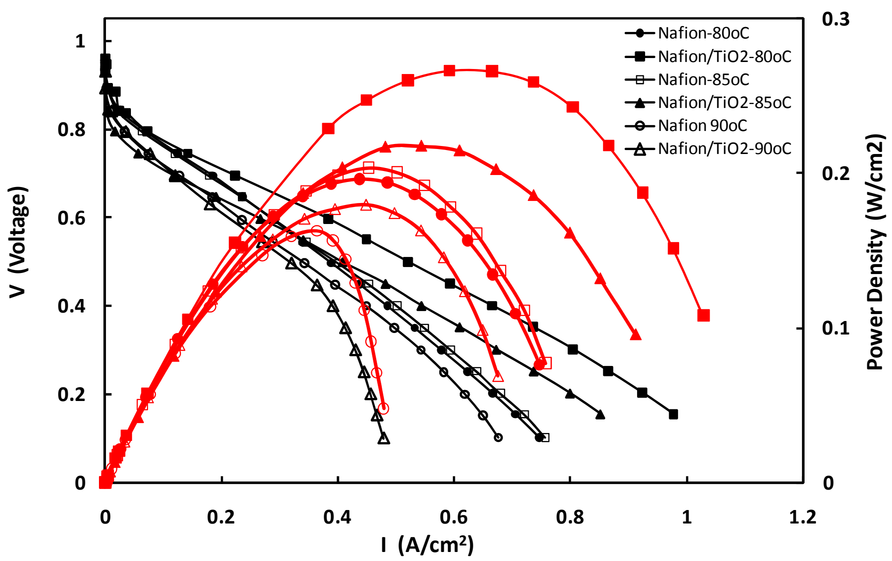

Figure 5: VI curve of Nafion and Nafion/TiO_2 composite membranes.

3 Conclusion

Nafion/TiO_2 composite membranes prepared with TiO_2 nanoparticles exhibit 30% higher power density compared to Nafion membranes. The maximum power density achieved is 0.266 W/cm^2 at 80^{o}C for composite membranes. Uniform distribution of TiO_2 nanoparticles in Nafion enhances the thermal stability of Nafion membranes. Although the power density decreases with increasing temperature above 80^oC, the composite membranes resist up to 110^oC in PEMFC. These results should be conducive to the preparation of new membranes suitable for PEMFC.

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