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The PROMETHEE multiple criteria decision making analysis for selecting the best membrane prepared from sulfonated poly(ether ketone)s and poly(ether sulfone)s for proton exchange membrane fuel cell

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ABSTRACT

Proton exchange membrane as the heart of fuel cell has been the topic of many research activities in recent years. Finding a suitable alternative for Nafion membranes is one of the most important issues of interest. This study is dedicated to sulfonated poly(ether ketone) and poly(ether sulfone) membranes. For synthesis of these two groups of polymers, two different isomeric biphenols (meta- and para-) were used and each group of membranes with three different degree of sulfonation (25, 35, and 45%) was synthesized. In this way, twelve different membrane samples were obtained and their properties were evaluated. Since each membrane had some strong and some weak points of properties in comparison to the other ones, using a rational analysis for choosing the best membrane between prepared samples was inevitable. For this purpose a PROMETHEE based multiple criteria decision making approach was applied and for evaluation of the weight of each criterion, Shannon entropy method was used. Final results showed that poly(ether ketone) membranes in selected criteria were better than poly(ether sulfone) membranes and as expected, membranes with the highest degree of sulfonation (45%) were placed at the top ranking levels.

1. Introduction

Fuel cells as devices for transforming chemical energy into electrical energy have been attracted much attention in recent years. Among several types of fuel cells, the proton exchange membrane fuel cells (PEMFC) are the most important ones. The heart of a PEMFC is its polymeric membrane that plays the role of electrolyte in the cell. Nafion applies as the polymeric membrane in most of today's commercial fuel cells. However, Nafion membranes show some disadvantages including high cost, limited operating temperature to 80 °C, and methanol crossover [1,2]. To overcome the obstacles, a great deal of research activities has been conducted to find suitable alternative polymeric membranes with lower cost and higher operating temperatures. Among the most prominent alternative polymers for preparation of membranes are poly(ether ketone)s and poly(ether sulfone)s [3–6]. Selection of monomers for preparation of polymers and consequently related membranes, with desired properties, has vital importance in final application. As, in a proton exchange membrane many parameters influence the efficiency and they are affected by the structure of the polymer and used monomers, selection of the best structure with suitable properties based on the parameters that sometimes are in conflict, is a challenging task.

On the other hand, in material selecting issue, the effect of different criteria and factors causes the decision making complex [7]. Multiple criteria decision making methodology (MCDM) is the suggested solution in such cases. MCDM is a discipline to make an optimum decision regarding vast and conflicting alternatives [8]. MCDM problems are divided into two main categories: multiple attribute decision making (MADM) and multiple objective decision making (MODM). The difference between two issues comes from their different purposes. MADM is applied in the evaluation facet facing limited numbers of pre-specified alternatives and preference ratings. MODM is specifically used for the design/planning, which

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considers to gain the goals regarding various interactions and constraints [9]. From another point of view, MCDM methods are classified as compensatory and non-compensatory methods. In compensatory methods, changes in a criterion value can be compensated, directly or reversely, by other values which are related to the others [10]. Non-compensatory methods acts reverse, not allowing lower values in some properties to be compensated by higher values in the others and penalizing the unbalanced data has been considered [11].

Significant applications of MCDM in various fields have been reported. One of the earliest methods is called AHP, "Analytic Hierarchy Process". AHP is developed by Thomas L. Saaty to analyze the complex decisions [12]. Similar to other MADM processes, it ranks alternatives considering the criteria. In energy issues, applications of AHP in hydrogen energy [13], solar energy technologies [14], assessment results and priorities for energy sector [15], and selection of electric power plants [16] were studied before.

Other important techniques are the "Technique for Order Preference by Similarity to Ideal Solutions" (TOPSIS), the "Elimination and Choice Translating Reality" (ELECTRE), and "Preference Ranking Organization Method for Enrichment Evaluation" (PROMETHEE).

TOPSIS was developed by Huang and Yoon. It determines ideal and negative ideal solutions and compares Euclidean distance of each alternative from them. TOPSIS assumes that the selected alternative should have the farthest distance from the negative ideal solution [17]. In the polymer context, it is two reports of TOPSIS applications in optimization of quality of polypropylene yarn [18] and selection of metallic bipolar plates for polymer electrolyte fuel cell [10].

The next MADM technique is ELECTRE. It finally takes an alternative that is preferred over most of the criteria and does not cause an unacceptable level of discontent for any of the criteria. The concordance, discordance indices and threshold values are used in this method [17]. As an application in fuel cell studies, Shanian and Savodogo used ELECTRE for selection of bipolar plates for polymer electrolyte fuel cell [19]. Also it is used for design of sustaining renewable energies exploitation [20] and location of thermal power plants [21].

The last method which is discussed here is PROMETHEE. Developed by Brans, PROMETHEE is an MCDM method which performs a pair-wise comparison of alternatives to rank them with respect to some criteria [17]. Briefly, the PROMETHEE method is implemented in hydrology and water management, business [22] and financial management [23], chemistry [24], logistics [25] and transportation [26], manufacturing [27], energy management [28], and social issues [29]. In fuel cell technology also some applications of MCDM methods have been reported [10,19], but lack of using an organized mathematical method for decision making in fuel cell membrane selecting is observed. In PROMETHEE method, using a way to evaluate the weights of the criteria is a necessity. In this study, the Shannon entropy method has been considered [30]. There are some studies of PROMETHEE in energy issue such as: ranking of alternative locations for small scale hydro plants [31], exploiting computational methods for planning and evaluating geothermal energy projects [32] and ranking of alternative energy exploitation projects [33]. To the best of our knowledge there is no report of PROMETHEE for selection of membrane in polymer electrolyte fuel cells.

In this work, for membrane preparation part, two series of sulfonated poly(ether ketone)s and poly(ether sulfone)s were synthesized. For synthesis of each series, two types of bisphenols with different structures were used and each group was synthesized in three different contents of sulfonation. In this manner, 12 types of sulfonated polymers were synthesized. To examine the prepared polymers, after casting and preparing membranes, some measurements were carried out. Proton conductivities at 25 and 80 °C, ion exchange capacity, inherent viscosity (as a measure of molecular weight of polymers), thermal stability, water absorption, glass transition temperature, and tensile strength were measured [34,35]. Fundamentally, each membrane with specific structure has its unique properties (e.g. mechanical, thermal, physical properties, etc.). As it was important that the selected membrane show acceptable properties in each criterion and also balanced data values, non-compensatory methods was taken into account. Among all of non-compensatory multiple criteria decision making methods, PROMETHEE II was selected because of its suitable uses of outranking methods and reasonable final results [7]. Accordingly, this paper describes an application of PROMETHEE II based on the Shannon entropy method for selection of the best membrane between 12 prepared membranes with different properties and different chemical structures for fuel cell application. Although the detailed structure and synthesis procedures of membrane preparation have been reported before [34,35], the summery of polymer synthesis and membrane preparation technique is expressed in the next section.

2. Membrane preparation

Sulfonated poly(ether ketone)s and poly(ether sulfone)s were synthesized via polycondensation of dihalide monomers with stoichiometric amounts of biphenol in the presence of excess amounts of potassium carbonate (Fig. 1). Two types of biphenols were used in which the orientation of substituents were different (BM and BP). Furthermore, the dihalide monomer for synthesis of poly(ether ketone)s was 4,4′-Difluorobenzophenone and for synthesis of poly(ether sulfone)s was Bis (4-fluorophenyl sulfone). Based on the ratio of sulfonated to non-sulfonated dihalide two series of copolymers with different degrees of sulfonation (25, 35, and 45%) for both poly(ether ketone)s and poly(ether sulfone)s were synthesized. In this manner 12 copolymer samples were obtained. In nomenclature of samples the first term shows poly(ether ketone) (k) or poly(ether sulfone) (s) and the second shows the type of used biphenol (BM (meta) or BP (para)), and the number represents the degree of sulfonation (1(25%), 2 (35%), and 3 (45%)).

For preparation of membranes, sulfonated copolymers in potassium salt form were cast onto a glass plate from their DMAc solution. The membranes were transformed to their acid forms by immersing in 4 M H_2SO_4 solution for 24 h. After that, the obtained membranes (in acid form) immersed in deionized water for another 24 h and were washed several times with deionized water. The obtained membranes dried in a vacuum oven at 60 °C overnight. All membranes which were transparent and flexible had the thickness in the range of 40–50 μm.

3. The proposed methodology

As mentioned, the PROMETHEE II and the Shannon entropy method was selected to find the best choice of proton exchange membrane.

3.1. The Shannon entropy weight method

The steps of this method were as follows:

1 Data normalization:

In the presence of n criteria and m alternatives, the original evaluation matrix, D, is constructed like: