ENERGY STORAGE & CONVERSION

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Cross-linked Sulfonated Poly(Ether Ether Ketone) Membranes for Fuel Cells and HVAC Systems

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The need to reduce pollution and the continuous increase in the fossil fuels cost, in addition to the continuous threat of nuclear energy also for political reasons, have strengthened the interest in efficient and clean systems for the conversion and storage of energy from renewable and easily available sources. This series aims to explore contributions to evaluate the state of the art and future developments in the field of rechargeable batteries, supercapacitors, solar cells, fuel cells, electrolysers and wave/tidal energy converter. Authors are invited to present their latest results, both original papers and reviews, focusing on the fundamental properties of the materials used, theoretical and experimental studies and their applications in green/blue energy.

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1. Introduction

Fossil fuels, such as petrol, carbon, and natural gases, supply a prominent part of the world's energy demand, and over the years the long-term consequences of their use are becoming unacceptable for the environment. In addition, these stocks are expected to run out in the next few decades. The International Energy Outlook 2013 report (IEO2013) [1] estimates a growth in energy consumption by 56% from 2010 to 2040. The total world energy use will rise from 524 quadrillion British thermal units (Btu) in 2010 to 630 quadrillion Btu in 2020 and 820 quadrillion Btu in 2040. The growth rate will be higher in the countries outside the Organization for Economic Cooperation and Development (i.e., non-OECD countries), where the energy demand is driven by a long-term economic growth, despite the economic crisis first, and the health crisis second, which is still sweeping the world with the Covid-19 pandemic. More specifically, in the period 1990-2040, energy use in non-OECD countries will increase by 90%, whereas in OECD countries the energy consumption will grow only 17%, with a continuous increase in the use of petrol, natural gases and especially coal. Note that, however, these data are subjected to fluctuations due to the varying economic, social and health conditions. Scientists and politicians are called to invest human and economic resources for the future towards the evaluation of promising and environmentally acceptable alternative energy sources [2].

To mitigate the greenhouse effect, it is necessary to identify highly efficient and environmentally friendly energy storage and conversion technologies. This is, indeed, the most important challenge for the sustainable development of human societies in the twenty-first century. For example, electrochemical devices, such as fuel cells, offer high efficiency not being bound by Carnot's theorem and reduced pollution coming from the internal combustion engine, avoiding the emission of polluting gases (CO_2, NO_x, etc). and microscopic particles (aerosols) having H_2O as the only emission. Unfortunately, their use is limited by labour costs and durability, which need to be more favourable factors to ensure large-scale applications. Remarkable advances have been made in the case of Li-ion batteries during the past decade, due to the massive investments made by car producers like Toyota and, more recently, Tesla motors, enabling the implementation of such devices in the automotive sector [3]. In 2019, the inventors of this technology, J.B. Goodenough, M.S. Whittingham and A. Yoshino, won the Nobel Prize in Chemistry [4]. However, Li-ion batteries still presents some limitations, such as low autonomy and long times of recharging [5]. A promising technology that could overpass these issues are fuel cells. In the past 30 years, fuel cells have received a lot of attention for their ability to use different fuels including hydrogen and/or alcohols (e.g., methanol), and for their high efficiency in converting chemical energy into electricity, since they are not limited by the Carnot cycle efficiency. In addition, they exhibit excellent environmental characteristics, with non-toxic emissions (only water as by-product). All these features allow a reduction in energy consumption and, at the same time, can contribute to the achievement of the commitment of the Kyoto Protocol in 1997 [6] (i.e., the first tool for negotiating internationally agreed standards for the reduction of greenhouse gas emissions by over 160 countries at Conference of the United Nations Framework Convention on climate changes [COP3]). The more recent commitment assumed by each country under the COP26 (Glasgow, 2021) to reduce greenhouse gas emissions and keep the increase in global average temperature below 1.5°C above pre-industrial levels in the next years, will be of vital importance [7].

In this book, the focus is a specific type of fuel cell comprising an ionomeric membrane that simultaneously separates the anodic and cathodic compartments, ensuring the flow of protons, i.e., the polymer electrolyte membrane fuel cells (PEMFCs), also called proton exchange membrane fuel cells. Such fuel cell operates at low (< 100°C) [8] or intermediate (100-200°C) [9] temperatures. Note that, though high operation temperatures have the main advantage of the reduction of carbon monoxide that otherwise poisons the catalyst (Platinum, Pt) in air [10], they promote the degradation of the polymer membrane and the loss of water, thus reducing the ion conductivity. The use of hydrogen allows to obtain high energy densities, making this system optimal for automotive applications [11].

On a different area, the housing construction sector is directed towards energy saving through significant improvements in the building insulation properties, and the recent tax incentives introduced by the EU and the governments of its Member States accelerated the renovation investments. Unfortunately, this solution leads to a decrease of outdoor air exchange, which induces the formation of indoor mold and increases indoor air pollution. On the market, there are many controlled mechanical ventilation systems, often combined with heat recovery devices. Using these devices avoids the arbitrary action of opening the windows for air exchange, while saving energy by pre-heating the cold outdoor air in winter with the indoor hot air coming out; in summer, the process is reversed. Some devices not only enable the heat recovery but can also humidify (in winter) and dehumidify (in summer) the indoor air (enthalpy recovery unit) [12] [13]. This effect is also useful for reducing the energy amount that air conditioning systems use to remove humidity from inside in summer and to increase it during winter. The interest in these devices has grown dramatically over the past few years, to the point where the European Union issued (July 2014) the Regulation 1253/2014 on the eco-compatible design of the ventilation unit [14].

In Fuel Cells (FCs) and Heating, Ventilation and Air Conditioning (HVAC) systems, the use of SAP membranes is promising, owing to the low cost of the polymer material, the easy and tuneable insertion of acidic groups on the polymer backbone, the high heat and humidity exchange ability (for HVAC), and the good proton conductivity (for FC). However, these systems present limitations in terms of degradation of their properties under certain conditions of operation of FCs, similarly to the case of Nafion. Nafion is an expensive perfluorinated polymer, and one of the major polymer electrolyte membranes (PEM) used for the fabrication of fuel cells [15-17]. For this reason, further studies are still needed to improve SAPs performance [18].

2. Sulfonated Aromatic Polymers (SAPs)

In recent years, aromatic hydrocarbon-based polymers are attracting great interest in various technological sectors. Among them, the sulfonated aromatic polymers (SAPs) are easily found on the market and are characterized by low production costs (the cost calculated for membranes with a thickness of 20 μm is about 4-6 €/m^2 and up to 20-30 €/m^2 for a thickness of about 100 μm). In addition, the amount of the acid groups on the polymer backbone can be easily tuned through aromatic electrophilic substitution reaction. They have good mechanical resistance, high thermal stability, good water retention, rapid response to changes in humidity and low gas permeability [18] [19]. The most studied precursors of the polymers belonging to this class are: poly(ether ether ketone) (PEEK), poly(ether sulfone) (PES), polysulfone (PSU) as shown in Figure 1 [20][24].

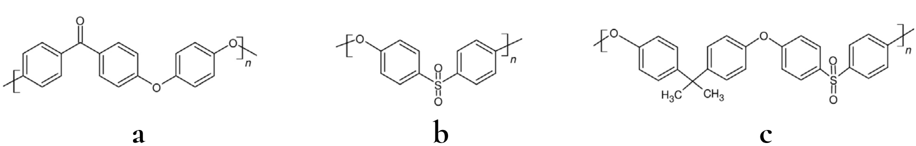

Figure 1. *Chemical structures of a) PEEK, b) PES, c) PSU.*

Series' Scientific Committee: Antonio Agresti, Maria Luisa Di Vona, Assunta Marrocchi e Riccardo Narducci.

Published works

1. Riccardo Narducci, Maria Luisa Di Vona, Assunta Marrocchi, *Cross-linked Sulfonated Poly(Ether Ether Ketone) Membranes for Fuel Cells and HVAC Systems*