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A new class of ionic electroactive polymers based on green synthesis

A. Aabloo [a], V. De Luca [b], G. Di Pasquale [c], S. Graziani [b,*], C. Gugliuzzo [c], U. Johanson [a], C. Marino [b], A. Pollicino [d], R. Puglisi [d]

[a] Intelligent Materials and Systems Lab., Institute of Technology, University of Tartu, Nooruse 1, 50411 Tartu, Estonia
[b] Dipartimento di Ingegneria Elettrica Elettronica e Informatica (DIEEI), Università di Catania, Viale A. Doria 6, 95125 Catania, Italy
[c] Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy
[d] Dipartimento di Ingegneria Civile e Architettura, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy

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In this paper, a novel class of ionic electroactive nanocomposites, named Ionic Polymer-Polymer Metal Composites (IP^2MCs) is introduced. IP^2MCs are capable of electromechanical transduction and, therefore, they are suitable to be used as nanocomposite artificial muscles. They represent an evolution of a class of totally polymeric ionic electroactive polymers, named Ionic Polymer Composites (IP^2Cs), previously proposed by some of the Authors. Compared to the parent technology, IP^2MCs exploit both the beneficial effects of electrodes based on polymeric conductors and the use of noble metal (Pt) nanoparticles. The deposition of platinum nanoparticles is obtained through a green chemical reduction process.

The fabrication process, and the influence of the novel nanocomposite electrode on the thermal, mechanical, and electromechanical behavior of green IP^2MCs are described together with a comparison with the properties of Ionic Polymer Metal Composites (IPMCs) and IP^2Cs. Reported results allow concluding that electroactive devices, with performances comparable with those of IPMC actuators, can be obtained. Eventually, the production procedure is more environmental friendly, cheaper and faster than the corresponding technique used for IPMC fabrication.

1. Introduction

Ionic Polymer–Metal Composites (IPMCs) [1–9] are Ionic Electroactive Polymers (IEAPs), capable of reversible electromechanical transduction. At least during the last two decades, they have been the object of a flourishing interest because of many attracting properties, such as large bending actuation under the effect of a low voltage signal (few volts), lightness and softness. More specifically, they are considered transducers relevant to be used both as soft actuators [10,11], artificial muscles [1,5], and sensors [12]. Nevertheless, they suffer for a number of shortcomings that have, so far, hindered their complete exploitation. Efforts have been devoted, e.g., in developing cheaper composites [13]. Also, researches have been described and demonstrated the possibility to change the bulk ionomeric polymer [14–17], or the solvent [18,19], in the attempt to avoid environmental unfriendly fluorinated composites or to obtain better electromechanic performance. Finally, research efforts have been devoted to the possibility of changing the conductor used for the electrodes, by depositing conducting polymers (CPs) on Nafion membranes [20]. More specifically, in [21–26] some of the Authors demonstrated the possibility to realize totally polymeric actuators, named Ionic Polymer-Polymer Composites (IP^2Cs). They are a result of the efforts to move from IPMCs to totally organic and cheaper transducers. As a matter of fact, in the case of IPMCs an ionic polymer membrane (e.g. Nafion®117) is metalized on both sides with a noble metal [4]. Platinum and gold are commonly used to realize the electrodes due to their high electrochemical stability and excellent electrical conductivity [2,3]. Besides to them several alternative cheaper electrode materials and their combinations have been explored [27], however, low electrochemical stability of these materials limits the cycle life of IPMC. Although platinum electrode, after prolonged cyclic deformation, can develop cracks with the consequence of a higher surface resistance that can affect the actuation performance of IPMC, while gold is more elastic and offers better mechanical durability, nevertheless the low stability of the gold complexes in aqueous solutions makes the electroless plating process rather complicated and expensive [28]. For this reason we chose platinum, to fabricate the electrodes. For the case of IP^2Cs, the electrodes are obtained by deposition of a CP (e.g. poly(3,4-ethylendioxytiophene)-poly(styrenesulfonate),

* Corresponding author.
E-mail address: salvatore.graziani@dieei.unict.it (S. Graziani).

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PEDOT/PSS) onto the polymeric membrane, so that all-organic transducers are obtained. The use of PEDOT/PSS allows obtaining flexible and soft electrodes [29].

Manufacturing techniques required to produce IPMCs are usually rather complex and expensive [1–4,13], while the procedure adopted to fabricate IP^{2}Cs is quite simple. In fact, if PEDOT/PSS is used as the CP, the electrodes can be fabricated directly on Nafion® by oxidative polymerization in situ of 3,4-ethylendioxytiophene (EDOT) and sodium polystyrene sulfonate (NaPSS, added to improve the solubility of EDOT). The polymerization is obtained in the presence of iron(III) nitrate [26]. This manufacturing process is fast (one day, instead of five days, as required for the IPMC fabrication) and cheap (0,37 €/cm^2, against 7,55 €/cm^2, as required for IPMCs).

As in other IEAPs, the transduction mechanism requires cations migration, along with solvent molecules (water molecules of the first and second solvation shells in the investigated case). In the proposed composites, the required ions are present as part of the molecular polymer structure of the IEAP (because of the Nafion® use). On the contrary, non-ionomeric CP based actuators [30–32] require ions that need to be supplied from some kind of reservoir for the conducting polymer electrodes. Such a reservoir is generally a solvent outside the device. This last geometry requires for the CP based transducers to be immersed in a solution [33]. Mobile ions can also be contained in a porous polymeric layer between the electrodes of a triple layer structure. To this purpose, IEAPs transducers, including CP composites, using ionic liquids, have been proposed and investigated in the literature [29,34–36]. Unfortunately, concerns exist on the adverse effects on the environmental and even on the toxicity of such compounds [37,38]. Finally, the possibility to use CP based transducers in air, by using solid polymer electrolytes, has been proposed in [39,40]. In any case, the fabrication of non-ionomeric CP based actuators requires laborious steps [41], while the devices proposed here are much easier to produce and more environmental friendly.

The role of the electrode structure on the IPMC electromechanical transduction has been deeply investigated in the literature and there is a consensus on the need to have both a low superficial resistance and a large capacitance value [19], while maintaining excellent mechanical characteristics. It is generally understood that Pt based electrodes are not the best solution. They cannot, e.g., face the large strains, which are imposed to the electrodes. Such strains originate because of the bending deformations, both during the acting and sensing modes of IPMCs. CPs can, therefore, represent a better candidate to realize the transducer electrodes and, therefore, to improve the electromechanical transduction performance of the transducers.

In last decades, a growing interest in the use of CPs with incorporated metal particles has been observed. The hybrid materials exhibit, in fact, improved performances in comparison to those of the CPs [42–49]. Nanoelectronic devices with superior performance can be therefore obtained. More specifically, the possibility to include metal nanoparticles of the Group 1 B in photopolymerized organic conductors has been demonstrated [50]. The photopolymerization has been recently further exploited to incorporate metallic nanoparticles into the electrodes of ionic electroactive composites, with the aim to improve their transduction performance [51]. In that paper, electroactive devices with polypyrrole-silver electrodes were proposed.

In this paper, the possibility of loading the electrodes of IP^{2}Cs, having PEDOT/PSS based electrodes, by using platinum nanoparticles, is introduced and a new class of materials, that will be called Ionic Polymer Metal Composites (IP^{2}MCs), is obtained. As a relevant result, IP^{2}MCs are realized by using green chemistry, giving rise to green IP^{2}MCs. Green chemistry aims at minimizing or eliminating the use of substances hazardous to human health and the environment. Consequently, green chemistry implements the use of chemical products and processes that reduce the need and generation of these kinds of substances [52–57].

Typical routes to produce metallic platinum involve the reduction of chloroplatinic acid (H_2PtCl_6), using as reducing agent formaldehyde (HCHO) [58–60], sodium borohydride ($NaBH_4$) or hydrazine (NH_2NH_2) [2–4]. Unfortunately, these procedures show some disadvantages because the reducing agents and boron residues may restrict the implementation of the synthesized Pt nanoparticles in the devices, and, moreover, hydrazine is a highly toxic compound. Recently, there has been a great interest in synthesizing metal nanoparticles using green chemistry principles. Relevant for the green production of nanoparticles are reagents such as vitamins, sugars, plant extracts and biodegradable polymers.

In the proposed green IP^{2}MC, the platinum is reduced by using L-ascorbic acid (AA, vitamin C) [61,62]. This is a natural antioxidant that acts as a non-toxic reducing agent with a mild reductive ability. During the green IP^{2}MC fabrication process, an excess of AA, high temperature (100 °C) and longer reaction time have been, therefore, used to improve the yield. Formaldehyde, has been also used, to realize IP^{2}MCs. This allowed for a comparative analysis among the performances of IPMCs, IP^{2}MCs and green IP^{2}MCs actuators.

The proposed IP^{2}MCs can be considered as hybrids between IP^{2}Cs and IPMCs, with electrodes able to follow the expected large deformations that such a class of electromechanical transducers can undergo. More specifically, the production procedure, and the influence of the novel nanocomposite electrode, on the thermal, mechanical, and electromechanical behavior of green IP^{2}MCs are described. A comparison, with the properties of Ionic Polymer Metal Composites (IPMCs) and IP^{2}Cs, is also given.

The following of the paper is organized as it follows: in Section 2, the fabrication procedures are described. In Section 3, the dependence of the properties of IP^{2}MCs as a function of reducing agent used are commented and compared with those of IPMC and IP^{2}C. In Section 4, final comments and conclusions are given.

2. Experimental

Devices have been realized starting from Nafion®117 (an ionic polymer membrane, with a thickness equal to 178 mm, produced by DuPont). All reagents are commercial materials (Alfa Aesar Company and Sigma-Aldrich Group) and were used without further purification. In all experiments, high purity deionized water was used.

2.1. Fabrication of actuators

IPMCs have been manufactured by three sequential primary plating phases. Each plating phase consisted in the adsorption, 20 h at room temperature, in tetrammineplatinum chloride solution ($Pt(NH_3)_4Cl_2$). The absorption phase was followed by a reduction step, carried out at 40 °C, using sodium borohydride ($NaBH_4$). Finally, a secondary plating phase, carried out using hydroxylamine hydrochloride (NH_2OH–HCl) and hydrazine (NH_2NH_2) as reducing agents, was performed at 40 °C. During both the primary and the secondary plating, polyvinylpyrrolidone (Mw = 10000, 0.001 M) has been used as a dispersing agent [1–4,8,9].

IP^{2}Cs have been obtained by in situ polymerization of PEDOT on Nafion®117 films. The polymerization was carried out at room temperature using 3,4-ethylendioxytiophene (EDOT) and sodium polystyrene sulfonate (NaPSS), in the presence of iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$). A stirring time equal to 1 h was used [26].

The IP^{2}MCs hybrids have been manufactured starting from IP^{2}Cs (see Fig. 1). The deposition on PEDOT/PSS of metallic platinum was