INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 2977–2987

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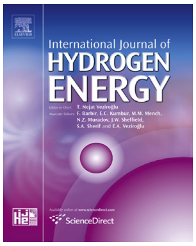

Properties of gel electrolytes based on PVdF/HFP containing anion receptors

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ARTICLE INFO

Article history:
Received 5 December 2012
Received in revised form
25 July 2013
Accepted 3 October 2013
Available online 5 November 2013

Keywords:
Polymer electrolytes
PVdF/HFP
Lithium salts
Anion receptor
Electrochemical properties

ABSTRACT

This work concerns systems utilizing gel electrolytes based on PVdF/HFP, containing a supramolecular compound additive. Supramolecular compounds are one of the many types of additives, and among them – anion receptors. Solutions of 1 M $LiClO_4$ or 1 M $LiBF_4$ in solvent: PC, PC/EC mixture (1:1), PC/DEC mixture (1:1) or EC/DEC mixture (1:1), were the liquid electrolyte encapsulated in a polymer membrane. *N*-[2-[Bis[2-*N*′-(3-pyridyl)ureido]ethyl]-amino]ethyl]-*N*′-(3-pyridyl)urea was applied as the supramolecular compound – anion receptor. Content of the receptor varied from 5 to 20 mmol in 10 cm^3 of 1 M lithium salt solutions. Changes in ionic conductivity and the stability of gel electrolytes – lithium electrode interface, were analyzed on the basis of impedance spectroscopy technique in Swagelok geometry. Lithium transference number was calculated for some of the studied gels using the polarization method. Finally, thermal stability of the systems studied was determined by means of DSC technique.

1. Introduction

Lithium based batteries showing good performance find broad application, from pacemakers and night-vision devices to mobile phones or notebooks. At first they were primary batteries, but within time extensive studies resulted in designing rechargeable batteries. The possibilities of these latter ones, first of all their multiple utilization encouraged researchers to further studies [1,2]. Various improvements have been introduced, e.g. the liquid electrolyte has been exchanged for a solid (polymeric) one. Polymer gel electrolytes are one of the examples of such electrolytes. The poly(vinylidene fluoride-co-hexafluoropropylene) copolymers may constitute the membranes for such electrolytes. They are assumed as a perfect alternative for traditional liquid electrolytes in application for lithium-ion batteries [3–9].

At present, studies are being carried out on improving the properties of polymer gel electrolytes by adding inorganic fillers [10–12] or supramolecular compounds [13,14]. The additives introduced may affect the electrolyte properties and when applied in batteries they will change their parameters. By introduction of appropriate amounts of desired supramolecular compounds better parameters of a battery are expected to be achieved.

When discussing supramolecular chemistry phenomena it should be noted that it is a field of short history, reaching only 50 or so years back. According to Lehn [15], this is chemistry dealing with intermolecular interactions and bonds, and also with associates of two or a larger number of chemical molecules or complexes.

Pedersen was one of the first who started work on supramolecular compounds [16]. In an experiment carried out by

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http://dx.doi.org/10.1016/j.ijhydene.2013.10.052

him, besides the main product – bis[2-(*o*-hydroxyphenoxy) ethyl] ether, also a byproduct – 2,3,11,12–dibenzo-1,4,7,10,13,16–hexaoxacyclooktadeka-2,11-diene was found.

This compound formed stable complexes with a large number of alkali and alkali earth metals ions. In the next years Pedersen carried out further studies on crown ethers, and in time calixarenes and other types of supramolecular compounds became of interest.

Artificial receptors can be classified according to the number of bonding sites. Therefore, they can be divided into anionic and cationic ones and into monotopic (forming supramolecular species only with one moiety) and polytopic ones (bonding two or more molecules) [15].

Anion receptors became of interest much later than cation ones, since the importance of anions in chemistry and biology was underestimated.

In order to bond anions, a molecule should bear groups (positively charged or neutral ones) characterized by electron deficiency. These will be first of all guanidine or ammonium groups (capable of forming M^+ N–H···X^- type bonds), centers showing electron deficiency (like boron or tin atoms), metallic centers in complexes, or groups which can utilize hydrogen bonds for complexing anions (e.g. –NHCO–, –COOH) [18]. The described group of compounds is additionally divided into those with a positive charge and neutral molecules. These latter ones may bond anions utilizing for this hydrogen bonds or ion–dipole interactions, or can coordinate them as Lewis acid centers [17].

In our laboratory, for some years now studies on anion receptors like calixarene [13] or calixpyrolle [14] have been carried out. It appeared that this type of receptors interact with I^-, $CF_3SO_3^-$ or $N(CF_3SO_2)_2^-$ type of anions, when PEO or PEG is the matrix. However, this type of anion receptor cannot be applied in PVdF/HFP based gel electrolytes due to the size of the matrix pores.

Therefore, an anion receptor of little less complicated structure was selected and hence of smaller dimensions. The receptor studied, the structure of which is presented in Fig. 1, is counted into the group of anion receptors.

The properties of the above compound were already studied [18]. It was found that complexes of it with $H_3PO_4^-$ are formed involving hydrogen bonds. It also appeared that the urea group is better for bonding this type of ions than the thiourea group. In another paper [19] data can be found that this ion is bonded selectively in the presence of HSO_4^- and Cl^-. This information is very important from the point of view of the receptor applied by us, since it confirms that this type of molecules is capable of bonding anions.

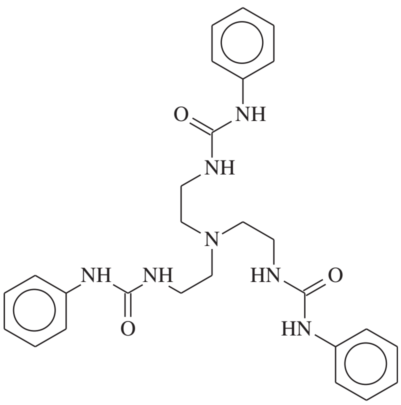

Fig. 1 – Structural formula of 1,1′,1″-(2,2′,2″-nitryltris(ethane-2,1-diyl))trisphenylurea).

The hitherto reports on another molecule differing from the one studied only with the substituent (it bears pyridine rings instead of phenyl ones) concerned utilizing it in aqueous systems [20–23]. It was found that various anions are bonded by means of hydrogen bonds. For example, for bonding the SO_4^- ion, eleven N–H···O bonds occurring between twelve NH groups and four oxygen atoms of this anion were utilized. It was found that each of the oxygen species is bonded by means of a different number of hydrogen bonds: the first one by four, the second one by 3, and the other two by two bonds. The metal cation accompanying SO_4^{2-} is coordinated by the nitrogen atom of the pyridinium ring by the so called second coordination sphere.

Custelcean et al. [22] studied also how SO_3^{2-}, SeO_4^{2-} and CO_3^{2-} ions are bonded by this supramolecular compound. From among the anions mentioned, only the shape of SeO_4^{2-} resembles that of SO_4^{2-} (it is only slightly larger). The results of the experiments carried out show that the complexes formed with the above anions are isostructural with that containing the sulfate (VI) ion. The only and at the same time small difference occurs in the spatial cell parameters. Further experiments carried out to estimate the receptor selectivity towards SO_4^{2-} confirmed this feature, and also allowed to determine the selectivity order. It is as follows: $SO_4^{2-} > SeO_4^{2-} > CO_3^{2-} > SO_3^{2-}$ and it is different than that expected.

The purpose of the work was to study the effect of the supramolecular compound additive on the physicochemical properties of PVdF/HFP based gel electrolytes. It seems to be a good anion receptor and hence should improve the physicochemical properties of the systems studied, even the most desirable lithium cations transference number. The electrolytes studied contained non-aqueous solvents and two types of lithium salts $LiClO_4$ and $LiBF_4$. In the work presented, this receptor was applied for the first time in non-aqueous systems and its interaction with ClO_4^- and BF_4^-. anions was studied.

2. Experimental

2.1. *Synthesis of anion receptor*

On the basis of the literature [21] and own experience, a method of receptor synthesis was elaborated. In a flask equipped with a magnetic stirring element, THF was introduced and tris(2-amineethyl)amine was dissolved in it. To the amine solution in THF, a slight excess of phenyl isocyanide was dropped in. The flask content was intensively stirred. After several minutes from completing dropping in phenyl isocyanide, precipitation of a white solid was observed. The reaction was carried out for still one hour. The post-reaction suspension was placed on a Schott filter and filtered under reduced pressure. The white solid was washed during filtration with small portions of THF. The product – white solid,