

Polypyrrole materials doped with weakly coordinating anions: influence of substituents and the fate of the doping anion during the overoxidation process

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Abstract

The influence of weakly coordinating anions with different shapes and substituents has been studied to get the overoxidation resistance limit of the material, ORL. The anions utilized are derivatives of $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$, $[\text{B}_{12}\text{H}_{12}]^{2-}$ and $[\text{B}_{12}\text{H}_{11}\text{NH}_3]^-$. The following tendencies have been established (1) boron cluster monoanions are to date the anions that offer the highest stability to overoxidation of PPy doped materials (2) the ORL stability of the material can not be attributed only to the shape of the cluster (3) monoanionic clusters are far superior than dianionic to get an ORL rise (4) cluster charge density reduction results in ORL rise as has been observed in $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ after incorporation of electron-withdrawing substituents with no electron back-donation (5) globular, rigid and large monoanions are less suitable for enhanced ORL values than elongated and non-rigid species (6) adequate anion's substitution produce a rise in the ORL of the material, thus polyether side-arms are beneficial with $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$, whereas, T-shaped methylaryl groups are appealing in $[\text{B}_{12}\text{H}_{11}\text{NH}_3]^-$ based materials, respectively, (7) substituents on the anions usually imply higher difficulty in the materials' growth. The high boron contents in these materials has permitted to learn on the fate of the doping anions during the overoxidation process. There is a built-up of the concentration of the doping anion in the electrolyte near surface area, whereas, a depletion is observed in the nearest inner layers.

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1. Introduction

Since their discovery 25 years ago, the development of conducting organic polymers (COP) combining organic polymer and semi-conducting electronic properties continues unabated [1,2]. Polypyrrole is one of the COPs most widely investigated regarding its potential applications [3] especially in sensors [4,5], actuators [6–8] or as electrochromic devices [9] among others. Polypyrrole materials (PPy) are reasonably stable in air, present high conductivity, good electrochemical properties and thermal stability and are easily generated both chemically and electrochemically [10]. For practical

applications, long-term stability of the material towards repetitive oxidation/reduction cycling or towards exposition to high anodic potential for short periods of time is of primary interest. The PPy chemical stability limit is known to be related to the overoxidation resistance limit (ORL) of the material, beyond which the conducting material properties are definitely lost [11,12]. It is generally accepted that during the PPy degradation process, nucleophiles usually attack the polymer double-bond alternating system, generating carbonyl groups, and producing the loss of the conductivity [13–16]. In the PPy electropolymerization, anions from the solution are inserted into the polymer matrix to maintain the material's electro-neutrality, neutralizing the positive charges generated on the oxidized polymer threads [3]. Therefore, the nature of the counter-ion used in the electropolymerization and the applied experimental conditions play a very important role in the resulting properties of the PPy films [17–19]. In the search for new properties, many investigations have been conducted on polypyrrole doped with different anions such as $[\text{ClO}_4]^-$ [20],

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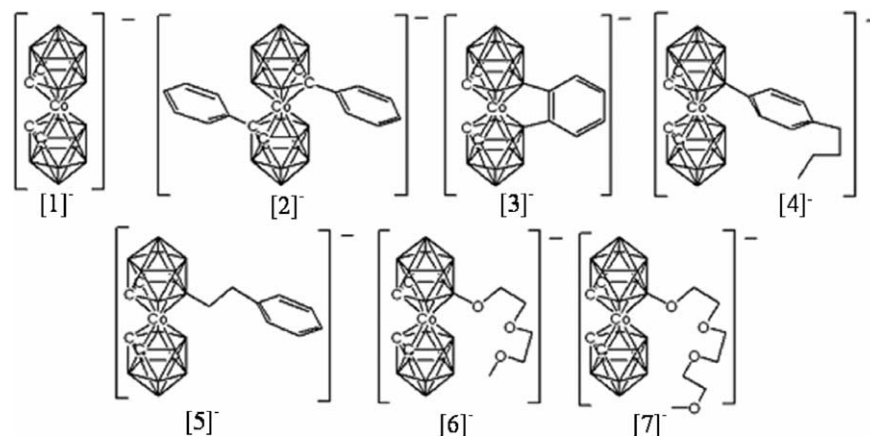


Chart 1. $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^{2-}$, $[1]^-$ and its derivatives $[2]^-$ – $[7]^-$. All plain vertexes are BH units. Vertexes simply named C stand for CH.

$[\text{BF}_4]^-$ [21], $[\text{PF}_6]^-$ [22], $[\text{NO}_3]^-$ [23], $[\text{Cl}]^-$ [23], surfactants [24] and even with unusual counter-ions like heteropolyanions [25] such as $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ or phosphotungstate [26] $[\text{PW}_{12}\text{O}_{40}]^{3-}$, among others. Weakly coordinating anions provide interesting properties in the fields where they are applied [27]. In particular weakly coordinating anions based on boron clusters have been successfully applied in many areas [28]. With the objective to study the convenience of using weakly coordinating anions derived from borane clusters in COPs we initiated the study on PPy [19,29]. Boron clusters appear to be very appropriate for this task due to their compact but not globular shape, the existence of exo hydride groups, and their low charge density. Interestingly $[\text{CB}_{11}\text{H}_{12}]^-$, the paradigm of the weakly coordinating carborane anions did not provide improved results with regard to conventional anions. Indeed $[\text{CB}_{11}\text{H}_{12}]^-$ and $[\text{B}_{10}\text{Cl}_{10}]^{2-}$ PPy doped materials gave ORLs up to 1090 and 890 mV vs. Ag/AgCl (10% KCl), respectively, values that are comparable to other data reported for common anions [29]. A definitive improvement in the ORL of PPy was found with the cobaltabisdicarbollide metallacarborane (Chart 1, $[1]^-$). This anion of formula $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^{2-}$ leads to a PPy material with an ORL of 1270 mV, practically 300 mV higher than previously studied PPy doped materials [19]. It is our interpretation that the elongated shape of $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^{2-}$, its low charge density and the spatial distribution of electron rich B–H groups which are hypothesized to interact with PPy positive charges should certainly be determinant in increasing the ORL. In this report we are presenting a thorough study of derivatives of $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^{2-}$ and the dinegative cluster $[\text{B}_{12}\text{H}_{12}]^{2-}$, $[8]^{2-}$, see Charts 1 and 2, to substantiate the above explanations in the unusual stabilization caused by $[1]^-$. These studies are complemented with monoanionic amino derivatives [30] of $[8]^{2-}$, Chart 2, in which there exists a dinegative cluster with a diffuse charge and a monopositive tail with hydrophobic groups.

These investigations emphasize the relevance of the B–H containing anions in enhancing the ORL of the PPy materials. Important improvements of the ORL values have been observed with the two series of borane anions studied, derivatives of

$[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^{2-}$ and $[\text{B}_{12}\text{H}_{11}\text{NH}_3]^-$. Divalent borane anions do not improve the ORL. Electronic effects in the sense to remove electron density from the cluster are proven to be relevant. Flexible side chains have produced the most overoxidation resistant materials for $[\text{B}_{12}\text{H}_{11}\text{NH}_3]^-$ derivatives, whereas, polyether side chains have produced the best in the $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^{2-}$ series. By XPS analysis assisted with Ar sputtering it has been possible to demonstrate the depletion of doping anions in inner regions of the material and the accumulation in near surface areas for PPy materials oxidized near the ORL of the material.

2. Experimental section

2.1. Chemical and reagents

Pyrrrole was purchased from Aldrich, distilled under reduced pressure before its use and stored under nitrogen at 0 °C in dark. The cobaltabisdicarbollide derivatives $\text{NMe}_4[3, 3'-\text{Co}(1-\text{C}_6\text{H}_5-1,2-\text{C}_2\text{B}_9\text{H}_{10})_2]$ ($\text{NMe}_4[2]$) [31], $\text{NMe}_4[8, 8'-\mu(1'', 2''-\text{C}_6\text{H}_4)-3, 3'-\text{Co}(-1, 2-\text{C}_2\text{B}_9\text{H}_{10})_2]$ ($\text{NMe}_4[3]$) [32], $\text{Cs}[3, 3'-\text{Co}(8-(1''-(4''-\text{C}_4\text{H}_9)-\text{C}_6\text{H}_4)-1, 2-\text{C}_2\text{B}_9\text{H}_{10})(1', 2'-\text{C}_2\text{B}_9\text{H}_{11})]$

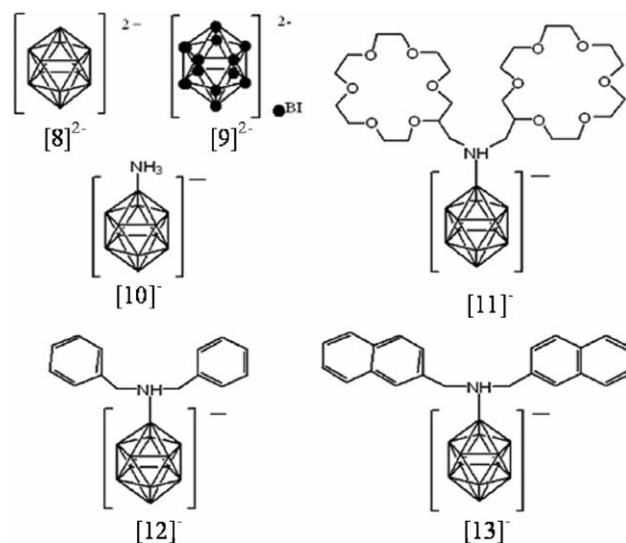


Chart 2. $[\text{B}_{12}\text{H}_{12}]^{2-}$, $[8]^{2-}$, and its derivatives $[9]^{2-}$ – $[13]^-$. All plain vertexes are BH units. Vertexes with a dark circle correspond to BI.

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