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Review

Vapour phase polymerisation of conducting and non-conducting polymers: A review

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ABSTRACT

Vapour phase polymerisation (VPP) is a well established technique in which the monomer is introduced to an oxidant-coated substrate in vapour form. Polymerisation then takes place at the oxidant vapour interface. VPP is a technique that could be used to immobilise materials to the modified electrode surface. This review article concentrates on the VPP of conducting polymers such as Polypyrrole (PPy) polythiophen (PT) and polyaniline (PANi). VPP of conducting polymers and other non-conducting polymers have extensively been investigated. This review article is divided into three main parts as given in Table of contents related to the VPP process of some important conducting polymers such as PPy, PT, PANi and Poly(3,4-ethylenedioxythiophene). A total of 181 references are cited in this review article and it attempts to look into VPP from inception of the method till present day.

Contents

1. Introduction

Polypyrrole (PPy), polyaniline (PANi), polythiophene (PT) are all π conjugated conducting polymers and are known as intrinsically conducting polymers (ICP). The usefulness of these conjugated polymers is a result of their ability to be deposited as thin films on to donor substrates. They are usually polymerised and simultaneously doped

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using electrochemical techniques in solution. They have attracted the attention of researchers in textile field due to their potential application in composite with natural, artificial or synthetic fibres. They have good conductivity, high stability and a good film forming property.

The conductivity of conducting polymers is attributed to the delocalisation of π-bonded electrons over the polymeric backbone, shows electronic properties, such as low ionisation potentials and high electron affinities [1,2]. They have attracted a great deal of attention in scientific activity in recent years as electronic conductors. Other applications include antistatic coatings, transparent conductors for display, organic thin film transistors, printed circuit, photovoltaic cells, smarts windows, capacitors and sensors. Conducting polymers have been widely used in the areas of bioanalytical science due to their inherent charge transport properties and biocompatibility [3,4]. Recently, conducting polymer nanomaterials have offered a great possibility for novel applications in synthesis and characterisation techniques [5–8]. Conducting polymers have been reviewed by many scientists especially in biosensor evaluations [9]. Some conducting polymers are doped and/or covalently or physically modified by nanomaterials [10] such as carbon nanotubes [11] graphene [12] metal nanoparticles [4,5,13]. They are also modified by bionano-materials [9,14], especially proteins [15], neurotransmitters [16], nucleic acids [17] and DNA [18] which exhibit unique catalytic properties that can be easily employed in the design of biosensors [19]. Conducting polymers have been used as impedance type gas sensors at low cost, highly sensitive and selective room temperature [6,7]. Serra et al. showed that conducting polymer sensors obtained by vapour phase polymerisation (VPP) are suitable for odour recognition [20]. Doping and undoping play key roles in the sensing mechanism of conducting polymer based sensors. Among these conducting polymers, PPy has superiority for commercial applications because of its unique properties [21].

Three polymerisation methods exist for conducting polymers. They are wet chemical oxidation, electrochemical polymerisation and VPP. VPP is a technique in which the monomer is introduced to an oxidant-coated substrate in vapour form. Polymerisation then takes place at the oxidant vapour interface as shown in Fig. 1. VPP can be either chemical vapour phase polymerisation (CVPP) or electrochemical vapour phase polymerisation (EVPP). CVPP is a solvent free process used to get uniform, thin and highly conductive polymer layer on different substrates. Stussi et al. described VPP as an innovative technological method that allows formation of layers of conducting polymers of any desired form and thickness in a uniform way on an insulating substrate [22]. The vapour phase deposition process has several advantages over other methods for depositing conducting polymers since the monomers are applied as vapour rather than a solution and there

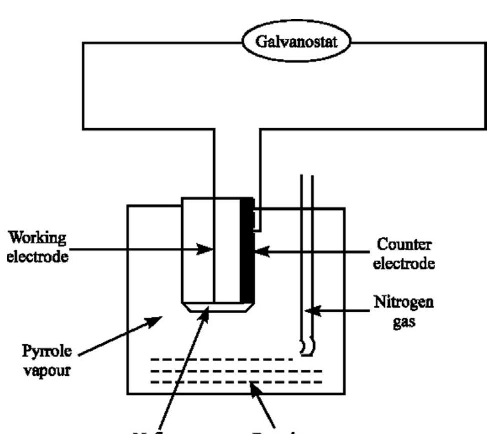

Fig. 1. Schematic diagram of vapour phase polymerisation cell [31].

is no liquid to act as transport medium for particle agglomeration. However, most conducting polymers suffer from insufficient conductivity which limits their use as current path in electronic devices. Intensive research has been conducted on VPP to overcome these drawbacks. ICP layers formed on the substrates via VPP have high electrical conductivity, and they are nearly agglomeration free because there is no liquid involved to act as transport medium. VPP also makes smooth homogeneous layer and VPP method is one way to achieve a clear thin film and a very smooth surface [23].

Spin coating, solvent casting or printing are other common techniques available for depositing thin and even polymer coatings. Most conducting polymers are difficult to process in this way because they have the major disadvantage of being insoluble in most solvents. Shin et al. have reported that dopants with long chains such as alkylbenzenesulfonic acids could overcome insolubility in most solvents with aniline, although polyaniline is produced by chemical polymerisation [24]. They also found out that the solubility and electrical conductivity of doped PANi increased with longer alkyl chain length of dopants. When PANi was doped with bulky alkylbenzenesulfonic acid, the solubilities were more than 80 wt% because the bulky dopants decreased interactions between polymer chains. The solubility of PANi increased with longer alkyl chain length of dopants because the longer alkyl chain acted as a better surfactant and increased free volume between polymer chains.

Mohammadi et al. conducted the first studies of VPP of conducting PPy using iron (111) chloride and H_2O_2 as oxidants at low pressure and several other researchers used normal pressure for their VPP [25–30]. Other researchers that have reported VPP technique for PPy include: Dallacqua, Lawal and Wallace, Subramaian, Winter Jean, Fu, Ueno and Uezu [26,27,31–35].

Fe(III) chloride and Fe(Tosylate)$_3$ are most common oxidants used in VPP [36,37], Fe(III) sulphonate [38], CuCl2 [39] and $HAuCl_3$ [40] have also been used as oxidants. Dopants (counter ion) that have been incorporated into conducting polymers (CPs) during electrochemical polymerisation and VPP include 2,4,6 trimethylbenzen, paratoluensulfonate, tiron, polyvinyl alcohol, methanesulfonate, octanesulfonate, butanesulfonate and polystyrenesulfonate [13,41–45]. Surfactants in solution and sulfonated dyes have been incorporated into conducting polymers as counter ion to induce interaction with particular proteins [46]. Complex and more delicate entities like antibodies or, enzyme [47–51] or carbon nanotubes [11,52–54] can also be directly incorporated as counter ions.

The use of ferric *p*-toluenesulfonate as an oxidant was initially reported by Ali et al. for the chemical polymerisation of 3, 4-ethylenedioxythiophene [55]. Subsequently, Fu et al. reported the use of Fe (III) *p*-toluenesulfonate as an oxidant for VPP on polyurethane foams [33]. Winther-Jean et al. used this same salt extensively as an oxidant for growing PPy and poly (3,4-ethylenedioxythiophene) (PEDOT) films by VPP [30,38,56]. Subramaian et al. used Fe(III) alkyl benzene sulphonate. In contrast to $FeCl_3$, Fe(III) *p*-toluenesulfonate does not crystallise as the solvent evaporates and this represents a significant advantage as it is necessary to suppress crystallite formation in the dried oxidant in order to obtain smooth PPy films [26]. VPP method can be used to deposit both PPy and PEODT even on non-conductive substrates, such as glass, PET and PES film surfaces. VPP have great advantages especially in PEODT processing, because there is no need to use poly(styrenesulfonate) (PSS) [57,58].

Functional polyelectrolyte such as dextrant sulphate, chondroitin and heparin act as dopants. They have been incorporated into polymer structure and they still retain their inherent bioactivity [59]. Nafion (perflorinated sulphonate), another polyelectrolyte also acts as dopant in solution and in vapour polymerisation [31,32,47,60]. Dopants