Current-Voltage Characteristics of Conducting Polypyrrole in Solid Polyethylene Oxide Electrolytes

S. RADHAKRISHNAN, SWATI UNDE

Polymer Science and Engineering, National Chemical Laboratory, Pune 411008, India

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ABSTRACT: Current-voltage characteristics were studied for polypyrrole films contacted with different electrolytes in aqueous form and complex polymer solid electrolytes. Cyclic voltammograms for the conducting polymer in aqueous medium exhibited the typical oxidation and reduction peaks, whereas for solid polymer electrolytes, there was large asymmetry in curves; with the anodic current being much higher than that in the cathodic region. A rapid switching-type response was noted in the case of polyethylene oxide-cupric chloride complex as solid electrolyte. This effect was pronounced when the same complex contained the polypyrrole deposited within it as a composite. These various results have been discussed in the light of different energy levels in the conducting polymer and the contacting medium, as well as the formation of a microdispersed system with higher charge transport. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2059–2067, 1999

Key words: conducting polymers; solid electrolytes; conduction mechanism; switching; I-V curves

INTRODUCTION

Conducting polymers have been attracting considerable attention in recent years because of their potential applications in devices such as electrochromic display, photoelectrochemical cells, optical switching devices, etc.^{1–5} The devices reported in the past make use of the conducting polymer film in liquid electrolytes (mostly nonaqueous), which may spill during handling or evaporate during long-term storage. To overcome these limitations, there have been attempts made in the past for replacing the liquid electrolytes with solid polymer electrolytes (SPEs).⁶⁻⁸ The SPEs are usually made by complexing a polymer, such as polyethylene oxide (PEO), polyvinyl alcohol, polyvinyl pyridine, etc., with inorganic salts such as lithium perchlorate, sodium, or potassium iodide. etc.^{9,10} These have been used as thin films

on the conducting polymer substrates and sandwich cell-type devices fabricated in the past, some of which were reported to be more efficient than others.^{11,12} However, the details of current-voltage characteristics (I-V) for these have been reported by only a few authors^{13–15} and only for specific electrolytes. During our investigation on such cells using conducting polypyrrole (PPy) films and PEO complexes as solid electrolytes, it was observed that the I-V characteristics were peculiar and their nature strongly dependent on type of the salt used for complexing with PEO. Further, switching type characteristics were noted when the PPy films were deposited *in situ*. Hence, detailed investigations were conducted on the I-V characteristics in PPy films contacted with SPEs, and the interesting results observed are reported in this article.

EXPERIMENTAL

The conducting polymer electrode was prepared by electrochemically depositing PPy on gold-

Correspondence to: S. Radhakrishnan.

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Figure 1 Schematic of the solid-state cell formed with conducting PPy film and SPE sandwiched between gold film backing electrode and ITO on glass substrate.

coated glass plates in the manner reported in the literature.^{3,4,16} A single-compartment electrochemical cell, with saturated calomel reference electrode (SCE) and platinum foil counter electrode in conjunction with computer-controlled potentiostat (Vibrant-EC 2010 system), was used for PPy deposition. An aqueous solution (0.06M)of pyrrole (Aldrich Chemical Co., Milwaukee, WI) with $0.1M H_2 SO_4$ was used as the electrolyte, and deposition was conducted potentiostatically at 0.7 V SCE for 2 min. The transparent conducting indium-tin-oxide (ITO) glass substrates (Corning Glass Works, Corning, NY) were coated with the SPEs consisting of PEO (Polyox WSR $M_W 3 \times 10^5$; BDH Chemicals Ltd., Poole, Dorset, UK) complexed with different alkali metal salts, such as KCl, KI, LiClO₄, NaClO₄, CuCl₂, etc., in a 4 : 1 molar ratio.⁹ The conducting PPy electrode and the ITO electrode coated with the solid electrolyte were sandwiched to form the solid-state cell (as shown in Fig. 1). The cyclic voltammetry (I-V) was then conducted using the same arrangement previously described (the reference electrode being the gold electrode in this case). All measurements were conducted at 35°C. In another set of experiments, the PPy films were dipped in liquid electrolytes as 0.1M solution of the salts previously described in distilled water, and their cyclic voltammograms were recorded using the three terminal cells with SCE as a reference electrode. A few of the SPE samples containing CuCl_2 coated on the ITO electrodes were exposed to pyrrole vapors to deposit PPy^{17,18} in them to form composite films. Gold films were deposited on these to make the sandwich cells that were also studied for their C-V characteristics in the manner reported elsewhere.^{19,20}

RESULTS AND DISCUSSION

The typical cyclic voltammograms or essentially current voltage curves (I-V) obtained for PPy films with gold electrode in aqueous electrolyte or in contact with SPE containing KCl are depicted in Fig. 2(a,b). It is seen that, in the case of aqueous electrolyte, there are two distinct peaks in the I-V at -0.4 V and -0.15 V corresponding to reduction and oxidation of the PPy accompanying undoping and doping of the film. On the other hand, in the case of PPy in contact with SPE containing KCl, there is a large anodic current superimposed on a small cyclic wave noted in the cathodic region. It may be mentioned herein that PEO-based SPE has comparatively high resistivity; thus, much lower current values are expected in these types of cells than those with the liquid electrolyte. Furthermore, it may be noted that the potentials in the case of SPE are with reference to gold, whereas those in liquids are with respect to SCE. The former are hence much higher ($\sim 0.8 \text{ V}$) than the latter. Nonetheless, there are distinct changes in the nature of the current voltage characteristics that are attributable to a charge transport mechanism other than just overall decrease of current (or increase of cell resistance). Furthermore, these differences observed are not just for the case of KCl, but also for other salts as well. The current voltage characteristics for the aqueous and PEO-based SPE containing LiClO₄, Na- ClO_4 , and Na_2SO_4 are shown in Figures 3, 4, and 5, respectively. It is seen that these also exhibit similar types of changes as those observed in the case of KCl when the electrolytes are changed from an aqueous one to an SPE type.

The most interesting results in the present experiments were observed for the samples containing CuCl₂. Figure 6 shows the I-V characteristics for the PPy films in aqueous and PEO-based solid electrolyte containing CuCl₂. The applied voltage in the case of the solid electrolyte has been raised because the overall resistance of the cell was high due to low conductivity in the SPE. The distinct differences in the I-V characteristics in the latter case are quite evident. There are sharp steps in the current at a certain applied potential in both increasing and decreasing cycles. These characteristics are suggestive of switching type behavior from a nonconducting state to a conducting state of the material. These type of characteristics were prominently observed for the SPE with CuCl₂ containing PPy deposited in situ by exposing the films to pyrrole vapors. Figure 7 depicts the C-V characteristics for such composite samples. It is clearly seen that there is a close similarity between these curves and those in Figure 6. It thus appears that the nature of the characteristics is



Figure 2 Cyclic voltammogram of PPy film in KCl electrolyte (a) aqueous and (b) as PEO complex solid electrolyte. Electrolyte concentration 0.1M for aquous and 4:1 mol/monomer unit for the solid PEO type. Scan rate 30 mV s⁻¹ SCE as reference electrode for (a) and gold for (b).

the same whether the PPy is contacted with the SPE in the film form or dispersed in the SPE as fine particles, but with a difference that in the latter case the current values are higher than the former.

The cyclic voltammetry of PPy films in liquid electrolytes has been studied by several authors, and it is well documented in the literature.²¹⁻²⁴ Although there are some changes in the actual potential values from one report to another, the overall features in the I-V are the same (viz. two peaks are observed in the I-V characteristics that correspond to the reduction and oxidation of the PPy films). This process of reduction and oxidation of the PPy is understood in terms of the transport of ions/charge carriers in and out of the polymer. The peak position and its sharpness depend on the nature of the dopant ion present in the electrolyte. The present observations for the PPy in liquid electrolytes are essentially in agreement with these reports. It is thus clear that freely mobile ions should be available for the doping/undoping process to take place, and these are present in the case of liquid electrolytes, whereas in the SPE, there will be less mobility of ions and

a different type of behavior would be expected. A few authors have mentioned the use of SPE, together with conducting $polymers^{13-15}$ and note similar I-V curves as in liquid electrolytes. Because the ionic transport in SPE is governed by the type/size of the ions, temperature, crystallinity, etc.,²⁵⁻²⁷ the similarity of the I-V curves would be observed only in certain cases where the ion transport is not hindered through the SPE (probably in $LiClO_4$ and $NaClO_4$), as well as the interface of SPE and conducting polymer. Large differences on the diffusion constants for the ions in SPE (of the order of 5×10^{-7}), compared with liquid electrolytes (> 3×10^{-5}), have been reported by Geng and colleagues.²⁸ Thus, one may expect the I-V characteristics to change at least in the value of currents and peak position when the SPE is used in place of liquid electrolyte.

In the present case, significant differences were noted in the I-V characteristics when the liquid electrolyte was replaced by SPE, with the latter exhibiting high anodic currents, compared with cathodic ones. There can be mainly two reasons for this type of behavior: (1) the charge transport across the PPy/SPE interface is easier



Figure 3 Same as Figure 2, but with $LiClO_4$ as the electrolyte.

in one direction than the other, and/or (2) the SPE allows transport of only one type of ion. In the SPEs, PEO is known to form complexes with al-

kali metal salts by binding the metallic ions within the helical matrix by coordination with oxygen atoms.^{9,10} Thus, it appears that one of the



Figure 4 Same as Figure 2, but with $NaClO_4$ as the electrolyte.



Figure 5 Same as Figure 2, but with Na_2SO_4 as the electrolyte.

charge species would be more mobile than the other in such electrolytes, compared with liquid electrolytes, wherein both the species are mobile. This may lead to the unusually nonsymmetric I-V characteristics observed in the case of SPEs. Furthermore, PPy has a work function of 5.0 eV,



Figure 6 Same as Figure 2, but with $CuCl_2$ as the electrolyte.



Figure 7 Current voltage characteristics for the solid-state cell containing the composite of PEO-CuCl₂ with PPy deposited *in situ*: (a) 4:1 complex and (b) 2:1 complex.

whereas the PEO has a work function of 3.95 eV.²⁹ This can give rise to a potential barrier for the charge transport at the interface, because of the mismatch in the energy levels in the two polymers. Thus, the charge transport across the interface of PPy and SPE is also quite different from that at PPy and liquid electrolyte. These various effects can give rise to the type of I-V characteristics described herein.

Now, considering the case of $CuCl_2$ complexed with PEO as the electrolyte, it may be noted that the rapid switching type characteristics were observed especially for those samples that were made by vapor phase deposition of PPy. In this process, the PPy formation takes place according to ref. 30:

$$N \operatorname{Py} + m \operatorname{CuCl}_2 \rightarrow [(\operatorname{Py})_x \operatorname{Cl}_{x-1}^-]_n + m \operatorname{CuCl}$$

where N (= nx) and m (= nx-n) are molar concentrations of monomer and dopant, respectively; and x is some fraction indicating dopant concentration in the polymer. The above equation is a more generalized form of that reported for x= 2.³⁰ This clearly suggests the formation of CuCl during the polymerization step. This component remains in the SPE during subsequent experiments and changes the nature of I-V characteristics. It may be of interest to note herein that the PPy has a work function of 5.0 eV, which implies that its valence band is 5.0 eV below vacuum level (0.0 eV), and the Fermi level that exists between bipolaronic states have been reported to be 1.7 eV apart above the valence band (i.e., at 2.2 eV below the vacuum level).²⁹ Furthermore, the Cu^{2+}/Cu^+ redox is expected at 4.653 eV below the vacuum.³¹ Thus, the transfer of electrons from the PPy bipolaronic state to the redox state in such a case is very much facilitated, whereas the reverse process is blocked. To confirm the role of CuCl, separate set of experiments were conducted by deliberately incorporating CuCl into the liquid electrolytes containing CuCl₂. Figure 8 shows the cyclic voltammograms for PPy in liquid electrolyte containing 20% and 30% CuCl (of total salt concentration). It is clearly revealed from these that the I-V characteristics exhibit additional waves that correspond to the oxidation and reduction of Cu(I) species. This wave becomes more pronounced and sharp with



Figure 8 Cyclic voltammograms of conducting PPy films in aqueous 0.1M CuCl₂ containing additional CuCl: (a) 10%, (b) 20%, and (c) 30% of CuCl. Other conditions are the same as in Figure 2.

the increase of CuCl [compare Fig. 8(a,c)]. At a high concentration of CuCl, the overall shape of the I-V resembles a sharp step-like characteristic similar to those in the Figure 6, with a difference that, in the latter case, the step is much steeper and the currents are much higher than in the case of PPy in liquid electrolyte. These differences in the I-V characteristics of Figures 6 and 7 can be understood as follows. In the case of PPy film immersed in liquid electrolyte containing CuCl₂/ CuCl [Fig. 6(a) and Fig. 8], there is a single junction formed at the interface of the polymer and the electrolyte, whereas in the case of PPy deposited in the SPE (Fig. 7) containing $CuCl_2$ (and in situ formed CuCl), there are a large number of such junctions formed at the PPv domains that are connected in series/parallel. Thus, the effect observed at each PPy-electrolyte junction gets amplified in the case of PPy deposited in the SPE, and one observes much higher current values, as well as a sharp step in their I-V curves. It may also be mentioned that the charge transfer to the redox sites within the SPEs is much more efficient when the electroactive component is dispersed in it.³² Hence, one would also expect a higher rate of charge transfer in the PPy/SPE composite than for discrete two layer structures. It may be of interest to mention herein that the differences in the I-V curves have been observed when the rate of charge transfer is much different than the rate of analyte transport near the electrode (e.g., in the case of microelectrode systems, compared with macroelectrode-based cells).³³ In the former, the I-V is sigmoidal, whereas in the latter it exhibits typical I-V peaks. The present results on the PPy/SPE composite cells seem to suggest that these behave more like microsystems in which each domain of PPy acts as a microelectrode on which the electrochemical reaction takes place.

CONCLUSIONS

The current-voltage characteristics for PPy in liquid and SPEs containing different salts have been studied. The cyclic voltammograms for the PPy in liquid electrolytes show the typical oxidation and reduction peaks corresponding to the doping and undoping of the conducting PPy. On the other hand, the cyclic voltammograms for the PPy film in contact with SPE have different features; in many cases, a very large anodic current is superimposed on a weak cyclic wave. In the case of electrolytes containing $CuCl_2$, entirely different behavior, suggestive of switching-type characteristics, is observed. This has been identified as due to the presence of CuCl in the SPE that is formed during the vapor phase deposition of PPy.

The present studies clearly bring out an important observation that the liquid electrolytes cannot be simply replaced by the corresponding SPEs, because this can change the current-voltage characteristics of the device. Furthermore, it would be preferable to disperse the electroactive component in the SPE rather than merely contact it externally. The dispersed systems give more efficient charge transport process than the sandwiched-layered type systems. This would be useful especially in chemical-sensing devices based on conducting polymers and electrolytes.

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