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Characteristics of plasticized PEMA/PVdF-HFP blend polymer electrolyte films doped with lithium triflate salt in electrochromic device

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Abstract

Poly(ethyl methacrylate), PEMA and poly(vinylidene fluoride-co-hexafluoropropylene), PVdF-HFP have been blended in the weight ratio 70:30. The blend has been doped with lithium trifluoromethanesulfonate (LiCF_3SO_3) and plasticized with ethylene carbonate (EC) and propylene carbonate (PC). The sample 70 wt.% PEMA/PVdF-HFP – 30 wt.% LiCF_3SO_3 exhibits room temperature ionic conductivity of $2.87 \times 10^{-7} \text{ S cm}^{-1}$. The highest conducting sample in the PC plasticized system is $1.46 \times 10^{-6} \text{ S cm}^{-1}$. The highest conducting EC plasticized system has conductivity of $1.05 \times 10^{-4} \text{ S cm}^{-1}$ and designated as 6EC. The plasticized electrolytes are transparent and mechanically stable at room temperature. An electrochromic device (ECD) with configuration glass/FTO/ WO_3 /sample/ CeO_2 - TiO_2 /FTO/glass utilizing S30, 6PC and 6EC as electrolytes have been fabricated. The cyclic voltammogram (CV) of glass/FTO/ WO_3 /6EC/ CeO_2 - TiO_2 /FTO/glass shows a cathodic peak occurring at -1.3 V upon coloration while an anodic peak is observed at -0.8 V during bleaching process.

Keywords: PEMA; PVdF-HFP; Conductivity, Cyclic voltammetry, Electrochromic device

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4 **1. Introduction**
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8 Polymer electrolytes have application in electrochemical devices such as supercapacitors [1],
9 rechargeable batteries [2], fuel cells [3] and electrochromic devices [4]. Polymer electrolytes are
10 safe, flexible, mechanically stable and can offer higher energy density as compared to
11 commercial liquid electrolytes [5].
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16 A gel polymer electrolyte (GPE) is formed when a low molecular weight aprotic solvent such
17 as ethylene carbonate (EC), propylene carbonate (PC), poly(ethylene glycol) (PEG) *etc* is
18 incorporated in a polymer matrix. GPE exhibits high ionic conductivity close to that of
19 commercial liquid electrolytes [6]. However, the mechanical strength of GPEs is lower compared
20 to dry solid polymer electrolytes (SPEs) [7].
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29 Electrochromic materials are capable of modulating their optical properties by gradually
30 undergoing coloration when voltage is applied, and recovers its original transparent state when
31 the potential is reversed [8]. Polymer electrolytes with ionic conductivity in the order of 10^{-4} S
32 cm^{-1} are acceptable for use in electrochromic applications [9]. Electrochromic devices can
33 function in less critical humidity conditions as compared to lithium ion batteries [10].
34 Electrochromic windows have been utilized successfully in automotive mirrors [11]. Other
35 applications include smart windows that are able to control heat transmission in buildings,
36 eyewears to provide comfort and safety, spacecraft thermal control and information displays [8].
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49 The good optical properties of poly(ethyl methacrylate) (PEMA) make it suitable for
50 application in electrochromic devices. PEMA-based polymer electrolytes for electrochromic
51 devices have been reported by Reiter et al. [12] and were found to exhibit good ionic
52 conductivity up to 10^{-4} S cm^{-1} . Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP)
53 contains both amorphous HFP and crystalline PVdF phases which provide plasticity and
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2.2. Preparation of solid and plasticized polymer electrolytes

0.7 g PEMA and 0.3 g PVdF-HFP were dissolved in 100 mL acetone. Different amounts (5, 10, 12.5, 15, 20, 25, 30, 35, 40 wt.%) of LiCF_3SO_3 were added into the solution and magnetically stirred vigorously under reflux for 2 h between 55 to 65 °C. LiCF_3SO_3 salt was heated at 130 °C for 3 h to eliminate any moisture prior to use. Plasticized polymer electrolytes were prepared by adding 2, 4, 6, 8 and 10 wt.% EC and PC into the highest conducting PEMA/PVdF-HFP – LiCF_3SO_3 composition. Upon cooling, the transparent solution was cast on glass plates and dried in an oven at 45 °C for several hours until dry transparent films were obtained. The films were stored in desiccator to remove traces of solvent and avoid moisture contamination before characterizations.

2.3. Preparation of the electrochromic device (ECD)

ECD was assembled by sandwiching the polymer electrolyte film between WO_3 working electrode, and $\text{CeO}_2\text{-TiO}_2$ counter electrode, with the two conducting surfaces of fluorine-tin oxide (FTO) facing each other. The configuration of the ECD is glass/FTO/ WO_3 /polymer electrolyte/ $\text{CeO}_2\text{-TiO}_2$ /FTO/glass.

2.4. Characterization techniques

2.4.1. Ionic conductivity

Impedance of the samples was determined using electrochemical impedance spectroscopy (EIS). The instrument used was Hioki 3531 Z HiTester. The measurements were done in the frequency range from 50 Hz to 1 MHz at different temperatures between ambient and 353 K. The impedance studies were carried out by sandwiching the polymer electrolyte film between

2.4.4. UV-Vis spectroscopy

UV-Vis transmittance measurements were recorded for WO_3 and $\text{CeO}_2\text{-TiO}_2$ electrodes and the electrochromic devices employing S30, 6PC and 6EC as ionic conductors. The transmittance spectroscopy was performed using low scanning speed with UV-1650PC Shimadzu spectrophotometer between 200 nm and 1100 nm. The electrochromic cell was placed perpendicular to the light beam of the spectrophotometer. Voltage was supplied to the electrochromic devices using a DC power supply which was connected through electrical probes.

2.4.5. Cyclic voltammetry (CV)

CV was carried out using CH Instrument Model 600D on the glass/FTO/ WO_3 /polymer electrolyte/ $\text{CeO}_2\text{-TiO}_2$ /FTO/glass electrochromic device to study the redox behaviors of WO_3 . The WO_3 working electrode will undergo coloration and bleaching upon the application of voltage. WO_3 coated on FTO was used as the working electrode, while $\text{CeO}_2\text{-TiO}_2$ coated on FTO was used as both the counter and reference electrodes. The potential range used was between -2.4 V to 0.7 V. The scan rate was fixed at 50 mV s^{-1} . The schematic diagram of the electrochromic device is shown in Fig. 1.

Fig. 1. Schematic diagram of electrochromic device configuration used during cyclic voltammetry study

3. Results and discussion

3.1. Conductivity measurements

The plot of ionic conductivity against amount of LiCF_3SO_3 is shown in Fig. 2.

Fig. 4. Effect of EC and PC content on the ionic conductivity at 298 K of PEMA/PVdF-HFP-LiCF₃SO₃ based polymer electrolytes

The ionic conductivity at 298 K for all the plasticized samples is higher than the polymer-salt sample. The polymer-salt complexes plasticized with EC exhibit higher conductivity over their PC plasticized counterparts. A maximum ionic conductivity was observed at 6 wt. % at $1.05 \times 10^{-4} \text{ S cm}^{-1}$ and $1.46 \times 10^{-6} \text{ S cm}^{-1}$ for the EC and PC electrolytes, respectively. The higher conductivity exhibited by the EC plasticized samples is due to the higher dielectric constant, ϵ of EC ($\epsilon = 89.6$) as compared to PC ($\epsilon = 64.4$). Hence EC should be able to increase the number density of ions from dissociation of the lithium salt [25]. The lower viscosity of EC ($\eta=1.90 \text{ cP}$) as compared to PC ($\eta=2.53 \text{ cP}$) [26] also helps to increase mobility of the conducting ions to diffuse more easily in the EC based electrolyte system. Hence, with the higher number of free ions expected from the EC plasticized system and the higher mobility of the free ions, the conductivity of the EC plasticized system should be higher than the PC plasticized system as obtained from our results. Similar observations were reported by Ali et al. [27] in PMMA-grafted natural rubber (MG30)-LiCF₃SO₃ polymer electrolyte system plasticized with EC and PC.

The degree of crystallinity of the plasticized samples can also contribute to the large difference in conductivity between the EC and PC plasticized samples, and thus was also investigated. Fig. 5 depicts the XRD patterns for plasticized samples 6EC and 6PC.

Fig. 5. XRD diffractogram of (a) 6EC and (b) 6PC.

Degree of crystallinity, α for both 6EC and 6PC samples was calculated using the formula

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4 The area under the curve of free triflate ions can be observed to increase when the amount of EC
5 or PC increased from 2 wt. % up to 6 wt. % which indicates increase in the number of charge
6 carriers, hence conductivity enhancement was achieved. Above 6 wt. %, the area of free ions was
7 observed to decrease for both EC and PC plasticized samples, which could explain the drop in
8 conductivity for compositions with above 6 wt. % EC and PC.
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19 **Fig. 8** shows the variation of ionic conductivity with $1000/T$ for salted and plasticized
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28 **Fig. 8. Temperature dependent ionic conductivity of S30, 6EC and 6PC samples**

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31 The temperature-dependent plots of all systems showed that the ionic conductivities
32 increased with temperature from 298 K to 353 K indicating that temperature helps to dissociate
33 the salt and produces more free lithium ions. The curved $\log \sigma$ versus $1000/T$ showed that both
34 EC and PC plasticized samples were non-Arrhenian and thus exhibited Vogel-Tammann-
35 Fulcher (VTF) behavior which implies that ionic transport is promoted by polymer segmental
36 motion based on free-volume model [33-34]. The VTF behavior is attributed to the amorphous
37 polymeric systems [35] and has been reported by many researches [36-41]. Ali et al [42] also
38 observed VTF behaviour for EC-plasticized and PC-plasticized MG30 samples.
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51 The plot for sample S30 on the other hand displays two linear sections with regression
52 values, $R^2 \sim 1$ below 308 K and $R^2 = 0.96$ above 308 K. The linear plots display Arrhenius-like
53 behaviour whereby two different activation energies, E_A were calculated using the Arrhenius
54 formula below:
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Using $T_0 = 244$ K for 6EC and $T_0 = 264$ K for 6PC, all points can be fitted to form a straight line with regression values, R^2 of ~ 1 , within limits of experimental error. The T_g value of 6EC sample is expected to be 20 K lower than 6PC. This big difference in T_g may also account for the large difference in ionic conductivity between EC and PC plasticized samples.

3.2 UV-Vis measurements

Light modulation capability of electrochromic devices is expressed by the transmission variation between the colored and bleached states. **Fig. 10** shows the UV-Vis transmittance spectra in the region between 400 to 700 nm for working electrode WO_3 , counter electrode $\text{CeO}_2\text{-TiO}_2$ and the electrochromic devices employing S30, 6EC and 6PC as ionic conductors.

Fig. 10. UV-Vis transmittance spectra between 400 to 700 nm of (a) WO_3 film and $\text{CeO}_2\text{-TiO}_2$ film, (b) glass/FTO/ WO_3 /S30/ $\text{CeO}_2\text{-TiO}_2$ /FTO/glass, (c) glass/FTO/ WO_3 /6PC/ $\text{CeO}_2\text{-TiO}_2$ /FTO/glass and (d) glass/FTO/ WO_3 /6EC/ $\text{CeO}_2\text{-TiO}_2$ /FTO/glass.

From **Fig. 10(a)**, the WO_3 layer showed high transmittance at 81 % in the visible range from 400 nm to 700 nm of the electromagnetic spectrum. On the other hand, $\text{CeO}_2\text{-TiO}_2$ layer showed an average transmittance around 74 %. The fabricated ECDs shown in **Fig. 10 (b) to (d)** displayed transmittance above 60 % at wavelength 550 nm and above. The maximum contrast of the ECD between the clear and coloured states in the visible region was found around the wavelength, $\lambda = 630$ nm. Light blue coloration occurred, thus the small contrast between the clear

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4 bleaching of the electrochromic window is slightly decreased with increasing cycles. This
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6 phenomenon indicates that the insertion and extraction of lithium that takes place between WO_3
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8 and CeO_2 - TiO_2 layers during cycling decreased slightly when the number of cycles of coloration
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10 and bleaching is increased.
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16 4. Conclusions

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18 Polymer electrolyte sample with composition PEMA/PVdF-HFP [70:30]: LiCF_3SO_3 :EC
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20 (65.8:28.2:6) has the highest conductivity of $1.05 \times 10^{-4} \text{ S cm}^{-1}$ at 298 K, which is mainly due to
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22 free ions dissociated from salt. FTIR and XRD results show larger number density of free ions
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24 and higher amorphousness in EC plasticized as compared to PC plasticized samples. ECD
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26 utilizing 6EC as polymer electrolyte has been successfully assembled and tested at ambient
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28 temperature. Change from transparent to light blue color of the ECD due to the insertion of Li^+
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30 ions into WO_3 layer is observed upon the application of voltage.
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38 Acknowledgements

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40 The authors would like to thank University Malaya for the research grant and L.N. Sim thanks
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42 the University for scholarship award.
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Figure 1

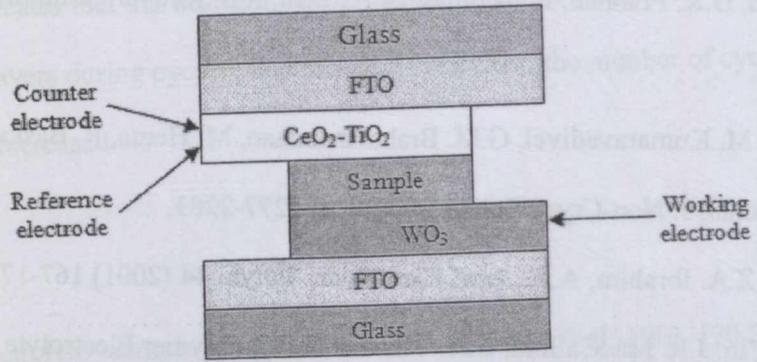


Fig. 1. Schematic diagram of electrochromic device configuration used during cyclic voltammetry study

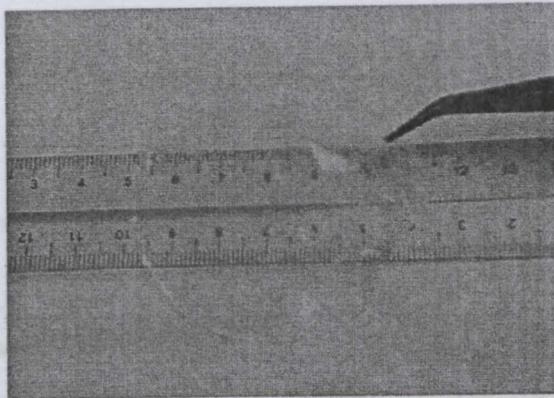


Fig. 3. Image of transparent PEMA/PVdF-HFP based polymer electrolytes

Figure5

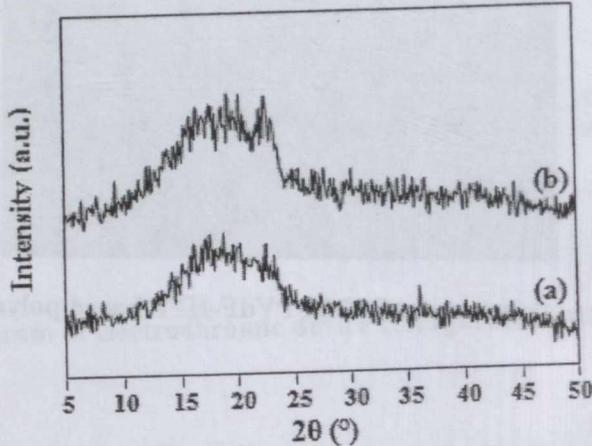


Fig. 5. XRD diffractograms of (a) 6EC and (b) 6PC

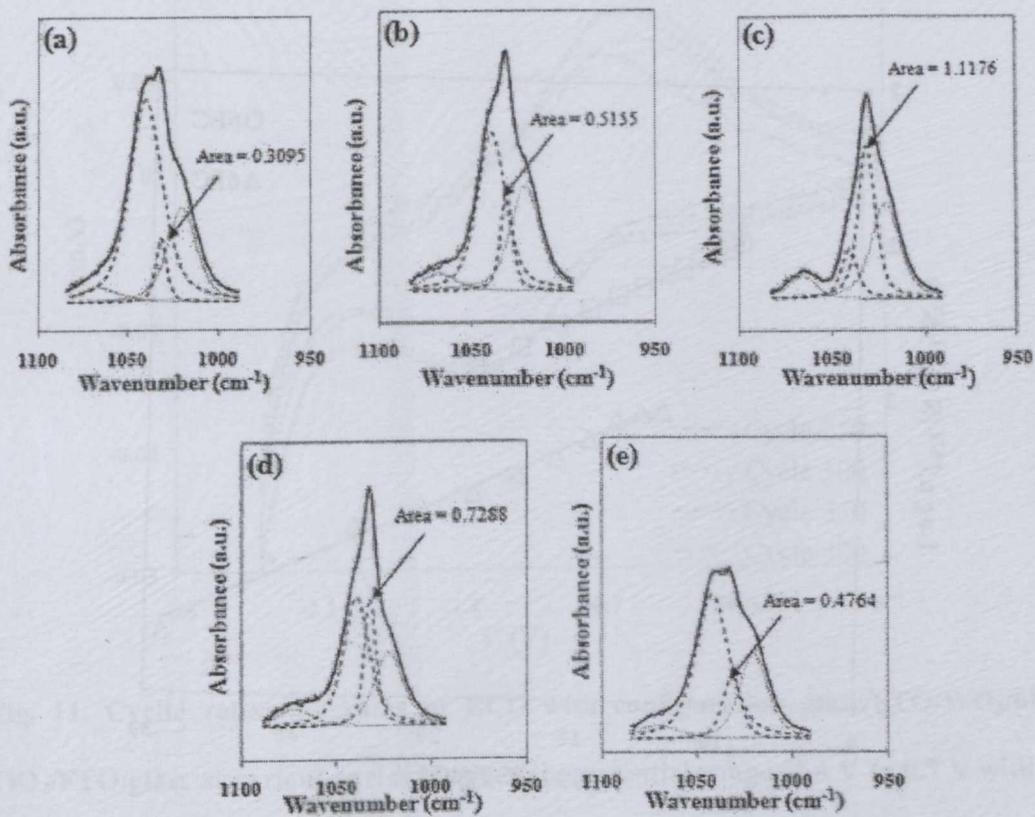


Fig. 7. IR deconvoluted bands between 1100 cm^{-1} and 950 cm^{-1} for samples (a) 2PC, (b) 4PC, (c) 6PC, (d) 8PC and (e) 10PC

Figure 9

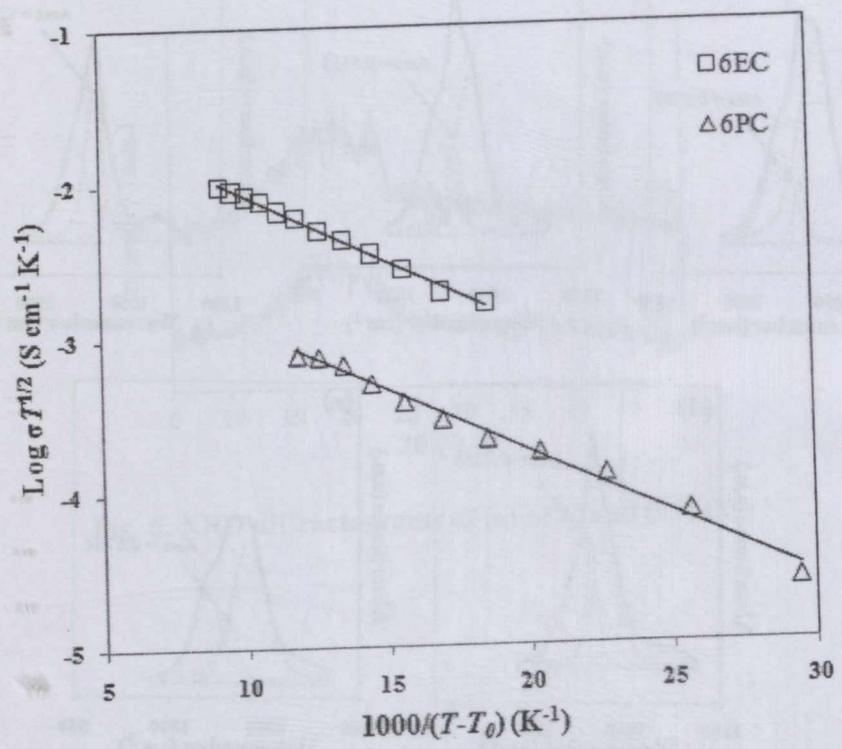


Fig. 9. Plot of $\log \sigma T^{1/2}$ versus $10^3/(T-T_0)$ for electrolyte samples 6EC and 6PC.

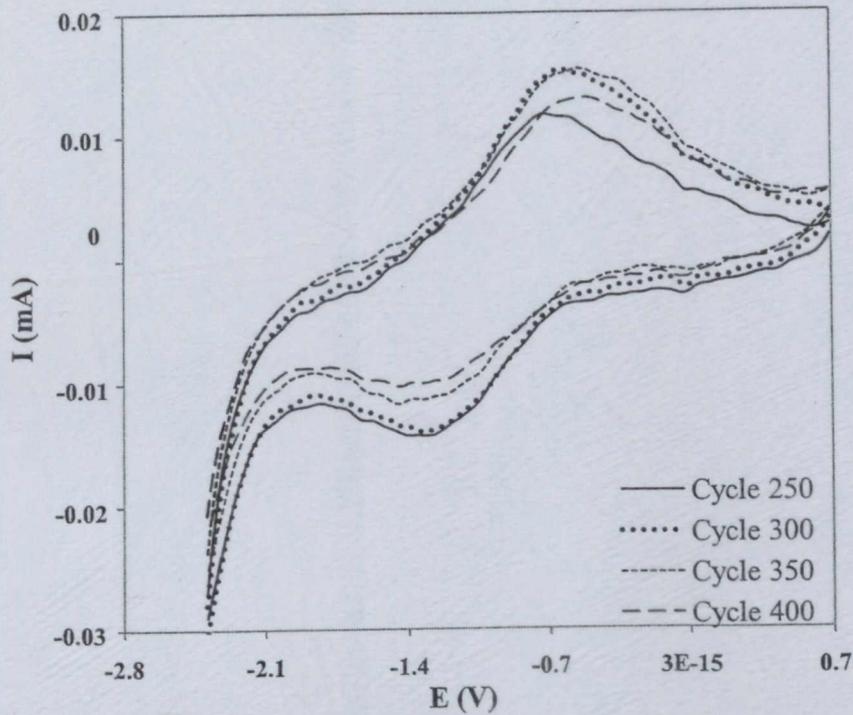


Fig. 11. Cyclic voltammograms of ECD with configuration glass/FTO/ WO_3 /6EC/ CeO_2 - TiO_2 /FTO/glass at various cycles between the potential range -2.4 V to 0.7 V with scanning rate = 50 mV s^{-1} .