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CORROSION BEHAVIOR OF ELECTROPLATED Bi COMPOUNDS WITH Se AND Te IN ETHYLENE GLYCOL BASED NON-AQUEOUS MEDIA

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În lucrare este prezentat un studiu despre coroziunea şi stabilitatea în etilen glicol şi în două lichide ionice (clorură de colină: etilen glicol, ChCl:EG) ale filmelor de BiTe şi BiSeTe depuse pe substrat de cupru. Comportarea la coroziune a filmelor de Bi a fost de asemenea investigată. Parametrii de coroziune au fost evaluați utilizând tehnicile de polarizare potențiodinamică şi spectroscopia de impedanță electrochimică (EIS). Datele Tafel şi EIS obținute în cele trei medii furnizează informații despre procesele şi structura interfețelor film-electrolit.

In this report a study about the corrosion and stability of the electroplated BiTe and BiSeTe films (on copper substrate) in ethylene glycol and two choline chloride based ionic liquids (choline chloride:ethylene glycol, ChCl:EG) is reported. Corrosion behaviour of Bi films in ChCl-EG systems was also investigated. Using both potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques the corrosion parameters were evaluated. Tafel and EIS data obtained in all three media provide information about the processes and structure of film-electrolyte interfaces.

Keywords: bismuth chalcogenides, corrosion, ethylene glycol, choline chloride, ionic liquids

1. Introduction

Studies about corrosion and chemical stability of semiconductor compounds of metals with tellurium (tellurides) and selenium (selenides) have relevance for thermoelectric (TE) and photoelectrochemical applications, in order to improve the efficiency of TE devices, optoelectronic devices and solar cells. Despite of numerous studies in aqueous media, the corrosion and chemical stability of such films in non-aqueous media have not been studied. The majority

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of papers solely focus on the synthesis process and composition analysis, and only rarely the characterization of stability properties is included [1] although there are many reasons to do this.

First, because TE devices can work frequently in non-aqueous media, especially as converters for energy harvesting in coolers and heat recovery from automobile exhausts. These devices can be immersed in various liquid or vapor media and generally the TE parts may be corroded since are polarized during their work. In solar cells field a major problem is also the photo-dissolution of semiconductor materials. Thus, the best chemical stability in such cells has been achieved by using non-aqueous solvents, which are less ionizing than water. In fact judicious selection of organic solvents for working media represents essential criteria pertaining to the increased stability and efficiency of devices. This essentially rests upon evaluation of the anodically polarized and induced corrosion in different kinds of liquids.

Moreover, TE materials or materials for solar cells have to be assembled when fabricating TE devices (modules). This requires the creation of contacts with suitable electrical, thermal and corrosion resistance properties. Therefore, the performances of a TE device depend to a great extent on the contact resistance between thermoelements (legs) and metal pads. It was shown, for example, that the electropolishing is a prerequisite step for cleaning the contacts with BiTe legs [2] and this operation may be well carried out in EG or ionic liquids [3].

A major reason for study the corrosion of selenides or tellurides is related to stability problems at their electrodeposition, because the chemical dissolution of freshly obtained films may occur during prolonged electrolysis. Literature shows that organic solvent containing baths are interesting since they have attractive features and yet can be operated at lower temperatures. Also, the non-aqueous baths as well as ionic liquid baths for electrodeposition of semiconductor compounds do not suffer from hydrogen evolution during the cathodic process. Lade *et al.* have prepared selenides [4] and tellurides [5] in ethylene glycol (**EG**) containing electrolyte. Ethylene glycol was used as organic solvent by Pandey *et al.* [6-8] during electrodeposition of some tellurides. Corrosion and dissolution of the anodes are also important subjects in these media, because the use of a soluble anode can be a suitable solution to prevent decomposition or contamination of the bath during prolonged electrolysis.

It has been shown recently that it is possible to create a ionic fluid by mixing quaternary ammonium halides with an amide, carboxylic acid or alcohol moiety. Combinations of choline chloride (2-hydroxy-N,N,N-trimethyl-ethyl-ammonium chloride, **ChCl**) with hydrogen-bond forming compounds, such as urea, malonic acid (**MA**) or ethylene glycol have recently been investigated and the resulted ionic liquids were studied as electrolytes for metal deposition and electropolishing [3,9]. As compared to ionic liquids containing imidazolium and pyridinium species, choline chloride based ionic liquids have low toxicity and are readily biodegradable. Furthermore, they are easy to prepare and cheap and therefore they hold promises for applications on a larger scale.

In this report a study about the corrosion and stability of Bi, BiTe and BiSeTe films by anodic polarization in an organic solvent (ethylene glycol, EG) and two choline chloride based ionic liquids (ChCl-EG) is reported. In order to study the above we have synthesized all films by electrochemical deposition on copper substrate. Both potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques were applied and the corrosion parameters were evaluated. We show that Tafel and EIS parameters obtained in different media provide information about the respective processes and structure of film-electrolyte interfaces.

2. Experimental

2.1. Deposition of Bi, BiTe and BiSeTe films

An aqueous electrolytic bath [10] containing 5M NaCl +1M HCl +10mM Bi_2O_3 was used during deposition for 1 hour of Bi-1 sample, with current density of $10 mAcm^{-2}$ and 25^0C temperature.

Table 1

Operation conditions for electrodeposition of Bi, BiTe, BiSeTe

Electrodeposited film	Electrolyte	Current density, mA/cm^2	Time, hours	Temperature, ^0C
Bi deposits				
Bi-1	5M NaCl + 1M HCl +10mM Bi_2O_3 (aqueous solution)	10	1	25
Bi-2	ChCl-MA (1:1) ionic liquid + 5mM Bi_2O_3	2	0.5	40
BiTe deposits				
BiTe-1	ChCl-MA (1:1) ionic liquid + 2.5mM Bi_2O_3 + 2.5mM TeO_2	electroless	0.67	65
BiTe-2 BiTe-3	ChCl-MA (1:1) ionic liquid + 1mM Bi_2O_3 + 2.5mM TeO_2	2.5 7	0.1* 0.1*	50 50
BiSeTe deposits				
BiSeTe	ChCl-MA (1:1) ionic liquid + 2.5mM Bi_2O_3 + 2.5mM TeO_2 + 0.5mM SeO_2	5	0.1*	50

*Rectangular pulsed current

The preparation of all other films [11] was performed from ionic liquids using either electroless procedure or electrolysis with current densities in the 2.5-$7 mAcm^{-2}$ range in pulsed regime at $50-65^0C$.

The bath consisted in an eutectic mixture of choline chloride : malonic acid (1:1 molar ratio) in which Bi_2O_3, TeO_2 and SeO_2 were dissolved in millimolar concentrations. Anhydrous EG (99.8%), ChCl and MA reagents were provided by Sigma Aldrich whereas oxides of Bi, Te and Se were purchased from Alfa Aesar. All chemicals were added as supplied, without further purification or drying.

A large Pt foil as anode was used in all experiments. After deposition the film covered electrodes were washed with Millipore water and air-dried. The preparation conditions of Bi, BiTe and BiSeTe films are described in Table 1.

2.2. Preparation of the solution for corrosion and corrosion testing

A conventional three-electrode set-up was constructed using a PTFE electrochemical cell for the corrosion study. The working electrode was placed horizontally at the bottom of the cell and sealed with an O-ring rubber leaving always an electrochemical active area of $0.636cm^2$. Opposite to the working electrode, a platinum coiled wire (with large area) was used as counter electrode and the reference electrode was an Ag/AgCl electrode (Metrohm) filled with 3M KCl electrolyte (211mV *vs.* standard hydrogen electrode at 20^0C).

The corrosive organic medium was ethylene glycol in which 0.07M tetra-buthyl-ammonium perchlorate (TBAP) was dissolved as supporting electrolyte. The corrosive ionic liquids consisted in ChCl : EG mixtures in two molar ratios, 1:2 (eutectic) and 1:4.

Current-potential polarization curves and EIS measurements were made at room temperature using a BioLogic Sci.Instr. potentiostat provided with a frequency response analyzer. Tafel potentiodynamic curves were recorded with scan rate of $1mVs^{-1}$ starting from open circuit potential (OCP). When plotting the polarization curves we take into account that prolonged anodic polarization might give rise to changes at the surface roughness which would imply parallel translation of the Tafel slopes. This effect was eliminated by first plotting the cathodic polarization curve and then the anodic one.

The linear polarization experiments were carried out with scan ± 20 mV *vs.* E_{OCP}. In the electrochemical impedance spectroscopic measurements frequency spectra were collected in the range of 1MHz to 50mHz with a sinusoidal signal of 10mV (rms) and film electrodes were anodically polarized up to 350mV overpotential.

3. Results and discussion

In order to evaluate the kinetics of the corrosion process for investigated samples we recorded the potentiodynamic polarization curves in semilogarithmic coordinates (Tafel curves). Figs. 1-3 give, as examples, the potentiodynamic polarization curves for Bi, BiTe and BiSeTe films recorded in three media: the pure ethylene glycol as organic medium and two ionic liquids containing also ethylene glycol in decreased concentrations.

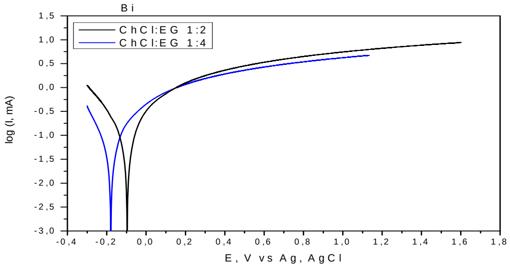


Fig. 1 The semilogarithmic polarization plots for Bi-1 film sample in two choline chloride based ionic liquids

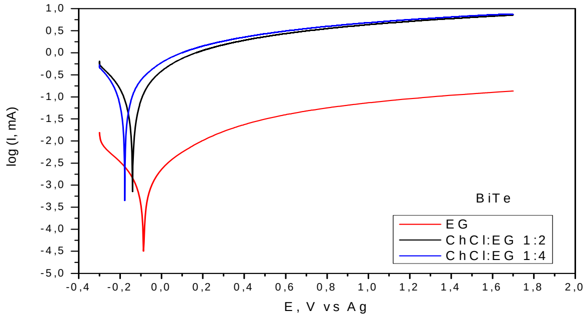


Fig. 2 The semilogarithmic polarization plots for BiTe-3 film sample in ethylene glycol and two choline chloride based ionic liquids

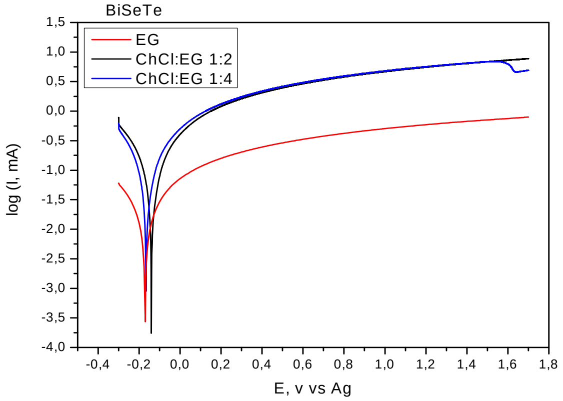


Fig. 3 The semilogarithmic polarization plots for BiSeTe film sample in ethylene glycol and two choline chloride based ionic liquids.

The cathodic reaction in the polarization curves obtained in ethylene glycol medium corresponds certainly to the beginning of the glycol electroreduction to its aldehyde. However, it is evident that the current in the cathodic branches of curves recorded in both ionic liquids corresponds to a more complex process. Besides the reduction of organic compounds (ethylene glycol and choline chloride) the evolution of the hydrogen is expected because when these ionic liquids hold in atmospheric conditions, the water content of the solutions is expected to be quite large, up to cca 10%. Therefore, the cathodic reaction may be assigned to reduction of EG, choline or trace water in the electrolyte, for water with the formation of hydrogen gas.

The anodic branches of polarization curves have the most important features related to the corrosion resistance. As can be seen from Figs. 1-3 the resulted current increased with more positive applied anodic potential and no obvious passivation occurred up to +1.7V polarization. However, for ionic liquids an increase of current at *ca.* +2.0 V (not shown in figures) would be most likely due to oxidation of Cl^- ion, provided by choline chloride. It is also expected for ethylene glycol with dissolved TBAP as the window of electrochemical stability to lie more positively than +2.0 V vs. Ag/AgCl, a potential when the electrooxidation of neutral EG molecules may takes place.

The corrosion parameters were calculated on the basis of potential-current characteristics in the Tafel region (E_{corr} ± 250mV) and listed in Table 2. Linear polarizations studied were also carried out; the slope of the line part of these plots in the vicinity of the corrosion potential (E_{corr} ± 30mV) yields the polarization resistance (R_p) for all studied samples and R_p values were estimated.

Values of the corrosion potential and corrosion current (E_{corr} and i_{corr}) were determined at intercept of extrapolated linear parts (Tafel lines) of polarization curves for each sample. The cathodic (*bc*) and anodic (*ba*) Tafel slopes were also obtained from the Figs. 1-3. Table 2 is representative of such evaluated kinetic parameters.

Table 2

The corrosion data for Bi, BiTe and BiSeTe obtained in EG, ChCl-EG (1:4) and ChCl-EG (1:2) systems using polarization curves, 1 mVs^{-1}scan rate; electrode surface: 0.636 cm^2

Electrolyte	Immersed film	Potentiondynamic curves				**Rp**, kΩ from linear polarization
		i_{corr}, μA	**E_{corr}**, mV vs.Ag/AgCl	Tafel slopes, mV/dec		
				b_a	**b_c**	
EG organic solvent + 70mM **TBAP**	BiTe-1	0.52	-102	250	220	16.72
	BiTe-2	0.36	- 90	200	212	29.45
	BiTe-3	0.17	- 98	188	187	58.41
	BiSeTe	8.53	-175	143	173	12.90
ChCl-EG (1 : 4) ionic liquid	Bi-1	31.20	-185	144	98	0.26
	BiTe-3	25.94	-105	140	113	0.30
	BiSeTe	83.23	-165	141	118	0.28
ChCl-EG	Bi-1	67.35	-104	159	133	0.36

(1 : 2) ionic liquid	Bi-2	80.00	-126	172	117	0.32
	BiTe-2	73.59	-142	129	109	0.36
	BiTe-3	42.00	-194	160	126	0.47
	BiSeTe	97.64	-147	147	94	0.48

As we consider comparatively the polarization studies with the BiTe and BiSeTe surfaces in EG solvent and in ChCl containing ionic liquids, different Tafel plots are obtained. Thus, the corrosion potential E_{corr} values for BiTe-3 with respect to Ag/AgCl reference suffer a substantially negative shift in the ionic liquid rich in ChCl (-194mV) compared to that in EG organic solvent (-98mV), which may be attributed to the involved liquid junction potential in the non-aqueous solvent; for BiTe-2 sample the difference is smaller (-90mV and -142mV, respetively).

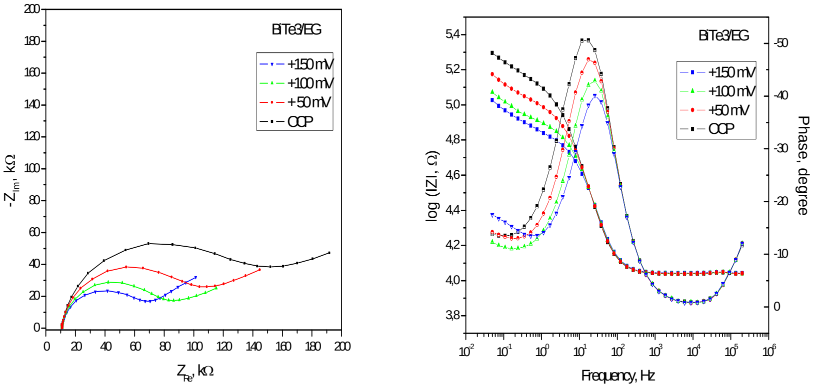
On contrary, for BiSeTe sample a moderately positive shift of the corrosion potential E_{corr} is recorded (-175mV, -165mV and -147mV, respectively). A possible explanation may be given by considering different electrochemical solubilities of tellurium and selenium in aggressive media. It appears that Se is more soluble than Te in EG, and this is confirmed by comparing the corresponding corrosion currents for BiTe and BiSeTe (0.17μA compared with 8.53μA). Thus, there is an anodic dissolution of selenium possibly as SeO_2 which goes into solution showing its acidic nature (H_2SeO_3 is formed in the presence of water traces). For bismuth and tellurium the anodic process in EG may lead to either their simple cations (Bi^{3+}, Te^{4+}) or to their oxides.

In Cl^- containing ionic liquids the corrosion currents are of the same order of magnitude for all samples regardless their chemical nature (Bi, BiTe and BiSeTe), but they increase with the content of choline chloride (Cl^-). Hence, the anodic dissolution rates in various media were found to be in the order:

$$\mathrm{EG} < \mathrm{ChCl(1{:}4)} < \mathrm{ChCl(1{:}2)}.$$

Regarding the Tafel slopes, the different values for b_a may be due to the different nature of molecules adsorbed on the electrode surface (ethylene glycol, chloride anion or choline cation). Also, the distribution of b_c values is hardly to be explained, but certainly an influence of water traces in all three media may have a great extent.

In other series of experiments, the electrochemical impedance spectroscopy (EIS) has been chosen as a very practical technique for investigating the corrosion behaviour of Bi, BiTe and BiSeTe films deposited on copper. In Fig. 4 we present, as an example, Nyquist and Bode spectra for BiTe-3 sample in ethylene glycol medium at open circuit potential and polarized at various anodic overpotentials.



(a) (b)

Fig. 4 EIS plots for BiTe-3 sample in EG at various anodic polarizations:
(a) Nyquist spectra; (b) Bode spectra. Surface area: 0.636cm^2

We mention that Nyquist and Bode plots for all other samples in the three investigated media (EG, ChCl:EG (1:4) and ChCl:EG (1:2)) have the same characteristics and they are not presented here.

As can be seen from Fig. 4, the Nyquist diagram shows at high frequencies a single semicircle which is indicative of a single time-constant, followed by a beginning of a straight line displaying an angle of about 45^0 to the real impedance axis at the low frequency range. The capacitive loop is certainly attributed to the charge transfer resistance during the anodic dissolution of films in aggressive media.

However, the Nyquist diagrams are not perfect semicircles and have depressed shape with centre under real axis and resemble as depressed capacitive loops. Such phenomenon often corresponds to surface heterogeneity which may be the result of surface roughness, dislocations, distribution of the active sites or adsorption of the molecules. The difference in real impedance at lower and higher frequencies (semicircle diameter) is considered as the polarization resistance (**R_p**) which may be a summation of all resistances at the film/solution interface. The R_p parameter is in a inverse correlation with corrosion current.

Table 3

The corrosion data for BiTe and BiSeTe anodically polarized in EG (+TBAP) using EIS method. Electrode surface: 0.636 cm^2

Deposited film	Anodic overpotential, mV, vs.Ag/AgCl	EIS parameters		
		Electrolyte resistance, **R_s**, kΩ	Polarization resistance, **R_P**, kΩ	Double layer capacitance, **C_{dl}**, µF
BiTe-1	0 (OCP)	11.15	46.5	10.2
	35	11.10	25.9	7.7

	50	11.04	13.1	8.4
	100	11.09	11.0	5.6
BiTe-2	0 (OCP)	10.40	145.0	3.8
	50	10.68	97.5	3.3
	100	10.72	74.0	2.7
	150	10.58	62.3	3.2
	200	10.86	51.2	2.7
	300	11.04	24.8	2.5
	350	10.95	26.6	2.4
BiTe-3	0 (OCP)	11.68	155.9	2.7
	16	11.53	120.0	3.1
	50	11.46	100.0	6.6
	100	11.50	70.0	4.5
	150	11.44	52.0	6.3
	200	11.45	46.2	2.9
	250	11.38	40.0	6.7
	300	11.40	38.3	5.2
	350	11.21	40.3	7.8
BiSeTe	0 (OCP)	8.37	12.74	56.8
	50	9.20	8.78	35.5
	100	9.22	5.31	40.0
	150	9.90	2.84	21.7
	200	9.19	1.58	58.0
	250	9.28	1.59	52.2

Table 4

The corrosion data for Bi, BiTe and BiSeTe anodically polarized in ChCl-EG (1:4 molar ratio) using EIS method. Electrode surface: 0.636 cm^2

Deposited film	Anodic overpotential, mV, vs.Ag/AgCl	EIS parameters		
		Electrolyte resistance, $\mathbf{R_s}$, Ω	Polarization resistance, $\mathbf{R_P}$, Ω	Double layer capacitance, $\mathbf{C_{dl}}$, μF
Bi-1	0 (OCP)	224	739	33.7
	40	227	142	60.8
	80	225	121	93.0
	180	226	73	85.4
BiTe-3	0 (OCP)	228	1540	219
	50	227	740	238
	100	227	427	235
	150	226	221	204
	200	226	185	296
	250	226	115	197
	300	226	111	270
BiSeTe	0 (OCP)	225	1895	382
	50	218	687	384
	100	216	238	414
	150	210	111	405
	200	209	80	346

	250	208	68	248
	300	207	45	270
	350	207	30	301

Thus, the diameter of the semicircle is the largest for spectra recorded at non-polarized electrode (OCP value, zero corrosion current) and decreases with increase the anodic overpotential. Correspondingly, the Bode diagrams show a gradually decrease of impedance modulus $|Z|$ when the electrode is anodically polarized. Values of R_p in all investigated corrosion cases are listed in Tables 3-5.

The straight line recorded at low frequencies may be interpreted by a diffusion controlled process at interface. Thus, the corrosion product layer behaves like a coating on the surface and creates a complex diffusion limiting barrier, although the product species are not adherent to the semiconductor film. The values $40\text{-}50^0$ of maximum phase angle exhibited by Bode diagrams are a support for this assumption; these values are more smaller than angle 90^0 that corresponds to a pure capacitive behavior.

Tables 3-5 present also values of ohmic resistance of electrolyte $\mathbf{R_s}$ as well as of double layer capacitance (C_{dl}) obtained using impedance modulus and substituting the value f=0.166Hz in equation (1):

$$|Z| = \frac{1}{2\pi f C_{dl}} \qquad (1)$$

Table 5

The corrosion data for Bi, BiTe and BiSeTe anodically polarized in ChCl-EG (1:2 molar ratio) using EIS method. Electrode surface: 0.636 cm^2

Deposited film	Electrode potential, mV, vs.Ag/AgCl	EIS parameters		
		Electrolyte resistance, $\mathbf{R_s}$, Ω	Polarization resistance, $\mathbf{R_P}$, Ω	Double layer capacitance, $\mathbf{C_{dl}}$, μF
Bi-1	0 (OCP)	188	267	13.3
	60	186	187	15.6
	100	198	151	17.3
	130	189	125	23.7
	280	182	108	18.5
Bi-2	0 (OCP)	185	165	25.3
	100	194	127	49.2
	130	205	119	79.4
	150	195	88	72.9
	170	189	74	61.6
BiTe-2	0 (OCP)	239	379	199.0
	50	238	302	269.0
	100	233	282	301.0
	150	241	213	272.0
	200	231	162	337.0
	300	240	134	277.0

	350	240	119	234.0
BiTe-3	0 (OCP)	242	781	340
	50	234	403	400
	100	229	364	480
	150	224	371	450
	200	224	342	430
	300	222	328	440
	350	222	319	450
BiSeTe	0 (OCP)	231	301	560
	50	220	239	640
	100	217	155	530
	150	214	106	470
	200	214	84	478
	250	213	79	529
	300	214	65	631
	350	212	61	463

From all three Tables it can be remarked a constancy of ohmic resistance of electrolyte during gradual polarization of electrode in a given electrolyte, but a huge difference, cca two orders of magnitude, between R_s values for working in pure ethylene glycol (5-6 kΩcm^2) and for working in ionic liquids containing ethylene glycol (around 120Ωcm^2, similar values for both ionic media). Knowing that R_s is a summation of electrolyte resistance, resistance of connectors and resistance of reference electrode, this difference may be attributed to the last one parameter.

As Table 3 show, the values of double layer capacitance C_{dl} for BiTe in EG solvent are in the range 3-8μFcm^{-2} and for BiSeTe are in the range 30-90μFcm^{-2}; this small differential capacitance appears to be the effect of EG organic aprotic molecules on the formation of double layer at the respective interfaces. From Tables 4 and 5, higher values of differential capacitance C_{dl} for all films in ChCl:EG ionic liquids can be noticed; these values of tents or hundreds microFarads per square centimeter are similar with those reported in the literature for representative ionic liquids [12].

4. Conclusions

Corrosion and stability of bismuth compounds containing tellurium and selenium studied by three electrochemical tests, as potentiodynamic polarization curves, linear polarization and impedance spectra at room temperature evidenced that corrosion performances depend on the aggressive solution and chemical nature of film. Some differences between corrosive non-aqueous media (pure ethylene glycol and two ionic liquids consisted in choline chloride: ethylene glycol mixtures) were found regarding corrosion parameters (E_{corr}, i_{corr}, R_p) as well as structure of interfaces (C_{dl}). BiTe films have lower corrosion current than BiSeTe or Bi films in all three media. The selenium component within the films is more susceptible to anodic dissolution than biemuth and tellurium. It was shown that electrolyte side of the interface plays a major role in the charge transfer during corrosion. These results are also useful in formulating the aspects of environmental pollution and the importance of recycling the toxic wastes of the TE devices and solar cells.

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