Cadmium (II) and lead (II) transport in a polymer inclusion membrane using tributyl phosphate as mobile carrier and CuFeO$_2$ as a polarized photo electrode

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ARTICLE INFO

ABSTRACT

In this work, a development of polymeric inclusion membranes for the cations separation is reported. The membrane was made up of cellulose triacetate (CTA) with a tributyl phosphate (TBP) incorporated into the polymer as metal ions carrier. The transport of lead (II) and cadmium (II) ions in two membrane systems polymer inclusion membrane (PIM), PIM coupled with photo-chemical electrode using TBP as carrier and 2-nitro phenyl octyl ether (NPOE) or tris ethylhexyl phosphate (TEHP) as plasticizer have been investigated. The membranes: polymer + plasticizer + carrier were synthesized and characterized by FTIR, X-ray diffraction and scanning electron microscopy (SEM). Transports of lead and cadmium have been studied using these systems and the results were compared to commercial cation exchange membrane (CRA). The obtained results showed that for Pb^{2+} ion, the concentrations of the strip phase increases using synthesized membranes. The conduction band of the delafossite CuFeO$_2$ (-1.25 V$_{SCE}$) yields a thermodynamically M^{2+} (=Pb^{2+}, Cd^{2+}) photo electrodeposition and speeds up the diffusion process. In all the cases, the potential of the electrode M/M^{2+} in the feed compartment increases until a maximum value, reached at $\sim$100 min above which it undergoes a diminution.

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1. Introduction

The separation processes [1] based on membrane technologies represent a sophisticated way for that purpose. The conventional routes, concern the synthesis of porous inorganic or hybrid membranes of well-defined pore size [2] or the modification of the surface properties in order to introduce specific interactions or electrostatic repulsive/attractive effects as in the case of membranes for electro dialysis [3].

The membranes modified by adsorption of polyethyleneimine and macrocyclic polyethers under the effect of an electric field showed an enhancement on their transport properties toward monovalent ions compared to divalent ones [4–6].

A solvent polymeric membrane which consists of a plasticizer polymer film has been used as example of liquid membrane containing a mobile carrier. Facilitated transport of metal ions through polymer inclusion membranes (PIM) has resulted in good selectivity in ion separations with vast improvements in membrane stability compared to over liquid membranes and polymer sta-

bilized liquid membranes [7,8]. The transport studies through cellulose triacetate (CTA) membranes as polymeric matrix with high flux and good stability have been recently reported [9–12]. We have developed a new plasticized cellulose triacetate membranes modified by carrier incorporation that are selectively permeable to copper and silver cations.

The separation and removal of toxic metal cations and neutral chemicals from water has frequently been addressed in membrane separation systems. Environmentally damaging and toxic cations have received significantly less attention primarily due to the challenging nature of selectively binding cations [13].

Tributyl phosphate (TBP) is widely used to separate toxic metal ions, particularly iron, zinc, nickel, chromium and copper [14].

Tributyl phosphate has been used to improve the wetting ability of mercerizing liquids and the film strength of lubricating oils [15]. Tributyl phosphate is a plasticizer and/or solvents for cellulose esters, lacquers, plastic and vinyl resins [16]. It is used as a solvent extractant of rare earth metals from ores [17]. This is an organic phosphor compound, which forms stable, hydrophobic complexes with metals such as cadmium and lead [18].

CTA membranes containing tributyl phosphate as carrier and 2-nitrophenyloctyl ether (NPOE) or tris ethylhexyl phosphate (TEHP) as plasticizers were prepared according to the procedure reported by Sugiura et al. [19–21]. The membranes polymer + plasticizer + carrier were characterized using chemical

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techniques as well as Fourier transform infrared (FTIR), X-ray diffraction and scanning electron microscopy (SEM). The permeation of lead and cadmium ions through CTA + TBP + NPOE membrane was comparable to that through a membrane in the presence of $CuFeO_2$ as polarized electrode.

Such study has been previously done using commercial cation exchange membrane (noticed CRA) and CdS as photo electrode for the separation and recovery of some metallic ions [22]. The behavior of such membrane has been investigated in different experimental conditions, for example in electrodialysis by using titane/platinium electrode [23,24].

On the other hand, there is an increasing interest in the photo electrochemically functional oxide materials. Considerable attention has been focused on developing new semiconductors (SC) for the photo electrochemical (PEC) conversion [25–28]. The delafossite $CuFeO_2$ has a gap E_g of 1.3 eV and absorbs in the whole sun spectrum. Additionally, it is low cost, non-toxic and exhibits a chemical stability over the entire pH range [29], these characteristics make it attractive for PEC applications.

The photo catalytic reactions are kinetically speeded down by a relatively slow charge transfer resulting in low conversion efficiencies. This occurs because the diffusion length, which is an intrinsic property, is small compared to the crystallite size and the lifetime of the minority carriers is not long enough to reach the space charge region by diffusion. Therefore, it is of interest to use $CuFeO_2$, elaborated by chemical route. The electrons must be captured by the metal ions and the distance they have to diffuse before reaching the interface is reduced below the diffusion length.

2. Experimental

2.1. Chemicals

$Pb(NO_3)_2$ (≥99%), $Cd(NO_3)_2$ (99.999%), chloroform (GC ≥ 99%), CTA (pure) and 2NPOE (GC ≥ 99.5%) were analytical grade reagents purchased from Fluka, tris ethylhexyl phosphate (GC ≥ 98%) was product of Merck. Whereas tributyl phosphate (GC ≥ 98%) was purchased from Aldrich. All reagents were used as received without further purification. The aqueous solutions were prepared by dissolving the different reagents in distilled water.

2.2. Membranes preparation

The CTA membranes were prepared according to the procedure reported by Sugiura [21]. A chloroform solution (20 ml) of CTA (200 mg), the appropriate plasticizer 2NPOE or TEHP (0.2 ml) and TBP (100 mg) were placed in 9.2 cm diameter flat bottom glass Petri dish. The solvent was allowed to evaporate slowly overnight to get a polymer film with a smooth looking surface. The obtained film was then carefully peeled out from the dish and placed in the transport cell with the side exposed to the air during evaporation facing the strip solution.

2.3. Analyses

The metal concentrations were determined by sampling at different time intervals aliquots (0.5 ml) from both the feed and strip solutions analysed with an atomic absorption spectrophotometer (Perkin Elmer 2380). IR spectra were recorded with Perkin Elmer spectrophotometer (Spectrum one). X-ray analyses were determined thanks to a Siemens diffractometer using monochromatized Cu Kα radiation.

A 5 kV scanning electron microscope (Hitachi S4500) was used to elucidate membrane morphology.

2.4. Ion transport

The cell used for transport experiments consisted of two compartments, made of Teflon with a maximum filling volume of 80 ml, separated by the PIM. The feed compartment contains the metal solution at a concentration of 10^{-1} M of metal salt; the strip compartment contains distilled water. The two compartments have the same volume 80 ml provided with a vertical mechanical stirrer with an agitation speed of 800 rpm which was previously determined as high enough to minimize the thickness of the boundary layer. The experiments began when starting the stirring motors in the two compartments. The exposed membrane area was 8.04 cm². All the experiments were performed in a thermostat at a controlled temperature of 25 °C.

In some homogeneous system, the mechanism of diffusion is based on the successive complexation/decomplexation from the feed to the strip compartment by electro hopping ion between the successive carriers present in the layer of the membrane.

With this mechanism, the transporters molecules act as stepping stones, and the solute moves through the membrane by jumping from one fixed site to another. The theory of fixed-site jumping was described by Cussler et al. [29] and Noble [30]. However, fewer systems have been characterized experimentally [30–35].

2.5. $CuFeO_2$ preparation

$CuFeO_2$ has been synthesized by nitrate way as reported in our previous work [25]; unreacted Cu_2O was removed by soaking the powder in NH_4OH (5 N). The end product exhibits a dark blue color and X-ray diffraction pattern revealed single phase. The electrode potentials were monitored by a Voltalab PGZ301 potentiostat and referenced with respect to a saturated calomel electrode (SCE). The solution (Na_2SO_4, 0.1 M) was continually desaerated by bubbling with nitrogen. The capacitance was measured as a function of the potential with a scan rate of 10 mV step^{-1}. AC voltage signal of 10 kHz in frequency and 10 mV peak to peak in magnitude was applied to the system. To facilitate the light transmission, the working electrode was irradiated by a 200 W tungsten lamp (Osram) positioned obliquely with an angle of 45°. In that position, the flux intensity, measured with a digital light meter (Testo 545) was determined to be 35 mW cm^{-2}.

3. Results and discussion

3.1. Physical and chemical characteristics of cellulose triacetate membranes

In Table 1, some characteristics of the membrane made up of carriers have been listed in comparison with those of the reference CTA membrane. As the carrier molecules (ionophore and plasticiser) are hydrophobic, the location of carrier molecules at the surface of the CTA modified membranes should modify the contact angle which is an indicative parameter of the wetting character of the material.

Table 1
Chemical and physical characteristics of cellulose triacetate membranes.

Membrane	Thickness (μm)	Density (mg/cm²)	Contact angle (°)
CTA	10	4.88	46.4
CTA-NPOE	15	6.12	80.5
CTA-TEHP	12	5.84	75.8
CTA-NPOE-TBP	23	6.65	77.2
CTA-TEHP-TBP	20	6.32	70.3

Table 2
Peak values and the corresponding radicals in different membranes. $m(CTA) = 0.2$ g, $m(TBP) = 0.1$ g, $\nu(TEHP) = \nu(NPOE) = 0.2$ ml.

Membrane	Peak value (cm^{-1})	Corresponding radical
CTA	3553	O–H
	2943	C–H
	1758	C=O
	1527	COO$^-$
CTA +TEHP + TBP	3476	O–H (CTA)
	2960	C–H (CTA)
	1756	C=O (CTA)
	1370	–CH$_3$ (CTA)
	1285	P=O (TEHP)
	1238	P=O (TBP)
	1026	P–O–C (TEHP)
CTA + NPOE + TBP	3476	O–H (CTA)
	2952	C–H (CTA)
	1754	C=O (CTA)
	1583	NO$_2$ (NPOE)
	1466	–CH$_3$ (NPOE)
	1357	C–N (NPOE)
	1264	P=O (TBP)

As shown in Table 1, the inclusion of carriers into CTA membrane induced an increase of its thickness. This increase generally parallels that of carrier molecular weight.

Our results showed that incorporation of TBP into CTA membrane give way to obtaining of a heterogeneous and amorphous PIM whose physical properties, such as thickness, density and hydrophobicity, modified.

3.2. Characterisation by FTIR

Table 2 collects the peak values and the corresponding radical of the reference CTA, CTA + NPOE + TBP and CTA + TEHP + TBP membranes. The obtained results showed the absorption band at $\sim$1754 cm^{-1} attributed to stretching vibrations of the carbonyl group. Bands at 1219 and 1055 cm^{-1} are assigned to the stretching modes of C–O single bonds. Less intense bands at 2944 and 2880 cm^{-1} are ascribed to C–H bonds whereas the wide band observed in the 3500–3100 cm^{-1} region is due to the O–H bonds stretching modes. The same table shows the bands at 1584 and 1608 cm^{-1} correspond to the stretching modes of C=C bonds of NPOE. The band at 1529 cm^{-1} is due to the stretching modes of –NO$_2$ bonds of NPOE. The bands at 1280 and 1043 cm^{-1} correspond to the stretching modes of C–O single bond. The above results showed that all the maximum values extracted from the spectrum of the CTA reference membrane, i.e. without plasticizers and carrier, are present in the modified membranes spectra in addition to those of the carrier molecules.

Thus, the CTA polymerisation process in presence of carriers should cause changes in intermolecular interaction of CTA chains. However, any sign for new chemical bonds between CTA and TBP using FTIR spectroscopy were observed.

3.3. Characterisation by X-ray diffraction

Based on the X-ray patterns of (CTA + NPOE), (CTA + NPOE + TBP), (CTA + TEHP) and (CTA + TEHP + TBP) membranes, the following observations can be drawn:

- The CTA membrane presents a single maximum located at $\sim$20° with a large broadening found in all polymers and corresponds to the van der Waals [36,37] halo. Thus, this material presents basically amorphous characteristics.
- The systems constituted by the mixture of CTA + NPOE, CTA + NPOE + TBP, and CTA + TEHP + TBP do not give any diffrac-

tion peak. It can be due to the absence of crystallisation within the membrane which permits us to eliminate the mechanism of transfer of the ions by successive jumps between carrier complexing sites in a 3D assembled state.

3.4. Characterisation by scanning electron microscopy (SEM)

The morphologies of CTA and CTA + NPOE membranes show that these membranes constituted by polymeric CTA present a porous structure, the distribution of the pores is nearly uniform. On the other hand, the CTA + plasticizer (NPOE or TEHP) and carrier (TBP) membrane present a dense structure where the pores of membrane have been filled by NPOE, TEHP and TBP molecules yielding a thick and less porous membrane.

3.5. TGA characterization of CuFeO$_2$ electrode

CuFeO$_2$ was characterized according to TGA measurements (Fig. 1). The first loss at $\sim$90 °C is originated from the water removal whereas the second one is due to nitrates decomposition of copper and iron respectively at 220 and 275 °C and which ends at $\sim$700 °C. The constancy of the mass beyond 800 °C indicates the beginning of the delafossite formation.

3.6. Photoelectrochemical characterization of CuFeO$_2$ electrode

The diffuse reflectance data were fitted to a direct allowed optical transition, the intercept of $(\alpha h\nu)^2$ with the $h\nu$-axis gave a gap E_g of 1.32 eV [28].

A great deal of attention has been paid on developing new semiconductors for the PEC conversion. The voltammogram of CuFeO$_2$ shows a small current density over a large potential range indicating a Schootky type nature of the junction (Fig. 2). The increase of the photocurrent (J_{ph}) along the cathodic polarization is characteristic of p-type conductivity. The constancy of J_{ph} under strong agitation implies that the electrons flow within the diffusion length is the rate limiting step. The Mott-Schottky characteristic was plotted at a frequency of 10 kHz:

$$\frac{1}{C^2} = \pm \frac{2}{e\varepsilon\varepsilon_0 A N_A} \left(V - V_{fb} - \frac{kT}{e} \right) \qquad (1)$$

All the symbols have their usual meanings and the sign '$\pm$' is relative to n- or p-type. The curve, depicted in Fig. 2 (inset), shows a linear behavior from which a flat band potential (V_{fb}) of +0.23 V and a hole density (N_A) of 1.58×10^{20} cm^{-3} were determined respectively from the intercept to $C^{-2} = 0$ and the slope. The negative slope
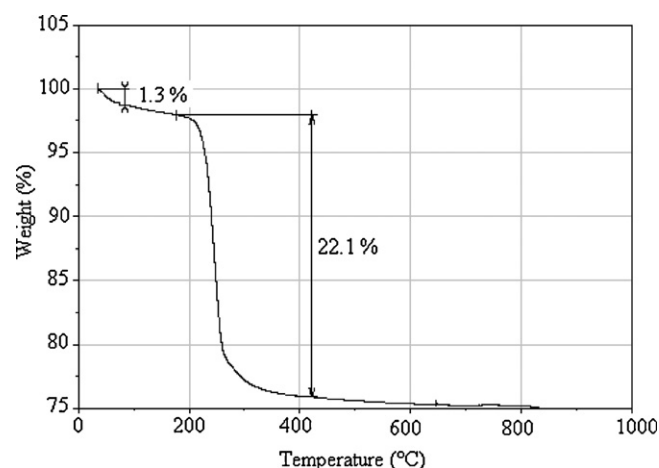

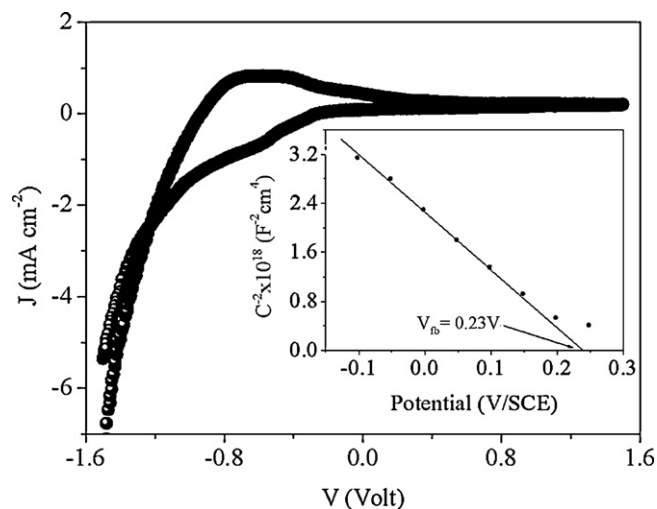**Fig. 1.** TGA curve of CuFeO$_2$ powder synthesized by nitrate way.

Fig. 2. The J(V) curve of CuFeO$_2$ plotted both in the dark and under illumination in KOH (0.5 M) solution; scan rate 10 mV s^{-1}. Inset: the Mott-Shottky characteristic determined at a frequency of 10 kHz.

indicates p-type character of CuFeO$_2$, attributed to oxygen insertion in the layered lattice.

3.7. Transport of metallic ions

3.7.1. Effect of the chemical nature of the plasticizer

The transport flux and its efficiency depend on the chemical nature of the plasticizer. An absence of transport flux has been noticed for some given plasticizers, presumably in relation with the values of the dielectric constant (ε_r) and viscosities (η); all the tested plasticizers ensure a significant transport flux when they act as solvents for supported liquid membranes (SLM) [38]. Fig. 3 shows the Pb^{2+} concentrations in a strip phase using TBP as carrier and two plasticizers.

It can be perceived that TEHP ($\eta = 10.2$ cP, $\varepsilon_r = 4.8$) and NPOE ($\eta = 12.8$ cP, $\varepsilon_r = 23.1$) produce the highest PIM transport of ions [39,40]. The polarity and viscosity appear to be the main characteristics of the membrane plasticizer which affect the PIM transport as previously outlined by Gardner et al. [41]. Indeed, the plasticizer polarity influences the chemical potential of metal ion partition-
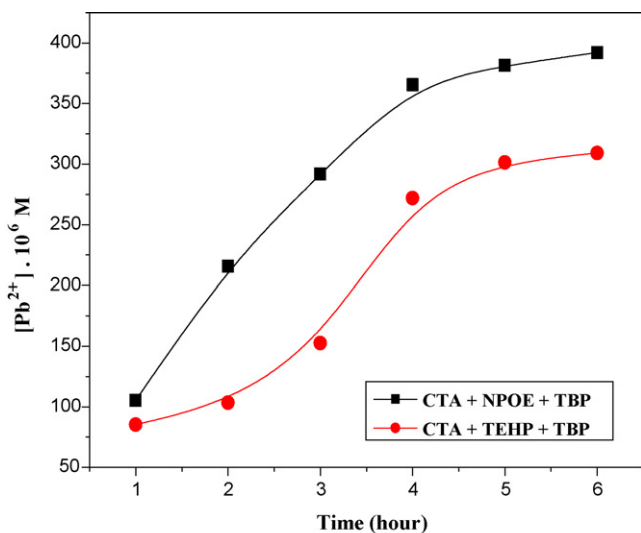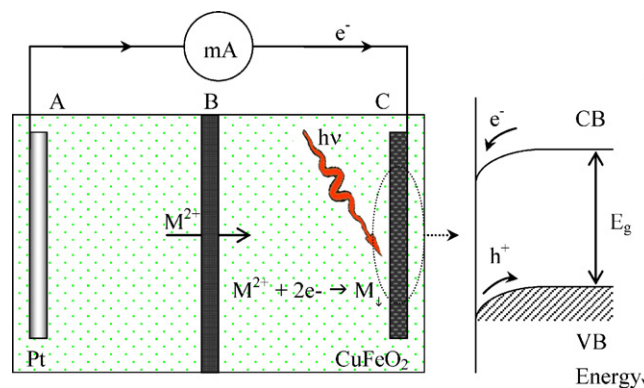

Fig. 4. Model of diffusion and photo electrochemical cell: (A) counter electrode; (B) membrane; (C) CuFeO$_2$ working electrode.

ing into the membrane, whereas increasing the viscosity of the plasticizer decreases the rate of transport, most likely by inhibiting the diffusion process. Kozlowski and Walkowiak [42] have found the same behavior when studying the Cr(VI) transport through PIM containing amines as ion carriers. These authors suggest that only high polarity plasticizers can be applied preferentially as solvent in PIM. More relevant papers published by the same research groups which specifically concern the separation of cadmium and lead using D2EHPA and Cyanex commercial extractants have found that the competitive transport led to a preferential selectivity for lead compared to cadmium [43].

3.7.2. Effect of the initial concentration of metal in a feed phase:

Table 3 represents the variation of the concentrations of Pb^{2+} and Cd^{2+} in the strip phase versus the initial concentration of ions. The results show that for weak amounts (10^{-5} to 10^{-2} M), the transport percentages is function of the feed initial concentration (transport percentages of metal ions increases sharply with the increasing the initial concentration of each metal in the source phase). However, beyond 10^{-2} M, the transport percentages tend to a maximal value (42.53–44.88% in the case of Pb(II) and 44.11–46.18% in the case of Cd(II)) and become independent of M^{2+} concentration. This is due to the saturation of the membrane by the metal–carrier complex molecules and the decomplexation at the strip interface is presumably the rate limiting step in such process.

3.7.3. Effect of membrane nature

The thickness, porosity and chemical nature of the membrane support are also fundamental operative parameters which can influence on the stability of the membrane and therefore the value of M^{2+} ion transfer flux. The dependence of the membrane nature has been studied using three supports of different physical characteristics. The results (Table 4) show that for Pb^{2+} ion, the concentrations of strip phase increases using synthesized membranes.

At equilibrium, the photo-voltage is limited by the band bending at the interface membrane/M^{2+} electrolyte (Fig. 4). A maximal value is therefore desirable in the darkness and is imposed by both the redox potential of the couple M^{2+}/M couple and the flat band potential V_{fb} of CuFeO$_2$. The ions M^{2+}, after crossing the membrane, were reduced owing to the redox potentials of the couple M^{2+}/M appropriately located with respect to CuFeO$_2$–CB. The M^{2+} ions diffuse across the membrane to be photo electrodeposited. The electrons move towards the auxiliary electrode via the external circuit where they reduce the ions M^{2+} to their elemental metal state. The conduction band (CB) of CuFeO$_2$ is mainly formed from the Cu$^+$: 3d orbital which provides a high energetic position and consequently a strong reducing ability. Its potential (-1.2 V) calculated from the relation

Fig. 3. Evolution of the concentration of lead in the strip phase versus time using two plasticizers NPOE and TEHP.

Table 3
Concentrations and transport percentages of lead and cadmium versus the initial concentration of metal after 6 h of experiments. Membrane: TAC + TBP + NPOE.

$[\text{Metal}]_{\text{initial}}$ (M)	$[\text{Pb}^{2+}]$ (M)	Transport percentages (%)	$[\text{Cd}^{2+}]$ (M)	Transport percentages (%)
10^{-5}	233.67×10^{-8}		303.95×10^{-8}	30.39
10^{-4}	349.46×10^{-7}	34.95	408.19×10^{-7}	40.82
10^{-3}	392.15×10^{-6}	39.22	424.54×10^{-6}	42.45
10^{-2}	425.28×10^{-5}	42.53	441.11×10^{-5}	44.11
10^{-1}	448.82×10^{-4}	44.88	461.82×10^{-4}	46.18

Table 4
Concentrations and transport percentages of lead and cadmium versus the nature of membrane after 6 h of experiments. $[\text{Pb}^{2+}]_{\text{initial}} = 10^{-4}$ M.

Membrane	Characteristics	$[\text{Pb}^{2+}]$ (M)	Transport percentages (%)
TAC + TBP + NPOE	Cellulose triacetate membrane	349.46×10^{-7}	34.95
TAC + TBP + NPOE with Electrode	Cellulose triacetate membrane + CuFeO$_2$	391.31×10^{-7}	39.13
CRA with Electrode	Polysulfone membrane + CuFeO$_2$	121.87×10^{-7}	12.19
Celgard 2400 with Electrode	Polypropylene membrane + CuFeO$_2$	143.27×10^{-7}	14.33

$(4.75 - V_{\text{fb}} + \Delta E)$[1] produces a large band bending value in presence of M^{2+} permitting an efficient separation of the (e^-/h^+) pairs in the space charge region and a charge transfer between $CuFeO_2$–CB and the $M^{2+/0}$ couple followed by M^{2+} photo reduction:

$$CuFeO_2 + h\nu \rightarrow h_{VB}^+ + e_{CB}^- \qquad (2)$$

$$2e^- + M^{2+} \rightarrow M \downarrow \qquad (3)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (4)$$

The electro-deposition catalyzes the diffusion process as proven by the concentrations of ions (Table 3) and the equilibrium (reaction (3)) strongly lies to the right hand i.e. metal deposition.

4. Conclusion

A cellulose triacetate membrane containing a tributyl phosphate as a carrier and 2-nitrophenyloctyl ether or tris ethyl-hexyl phosphate as plasticizers has been synthesized. These CTA + plasticizer + carrier membranes were characterized using chemical techniques as well as Fourier transform infrared (FTIR), X-ray diffraction and scanning electron microscopy. The systems constituted by the mixture of CTA + NPOE, CTA + NPOE + TBP, CTA + TEHP and CTA + TEHP + TBP do not give any diffraction peak. It can be due to the absence of crystallisation within the membrane. A comparative study of the transport across a polymer inclusion membrane (PIM) and a modified PIM by electrode containing the same carrier (TBP) in 2-nitrophenyl-octylether (NPOE) has shown that the lead transport efficiency was increased using modified PIM by electrode.

$CuFeO_2$ has been synthesized by chemical route in order to shorten the travelled carriers' path. The oxide crystallizes in the delafossite structure and absorbs over the whole solar spectrum in addition to being low cost and exhibits long-term chemical stability. The high energetic position of its conduction band is appropriately positioned to allow an efficient charge separation of the electron/hole pairs leading to metal deposition. The cations flow was considerably speeded up through the membrane with illuminated $CuFeO_2$ electrode followed by the electrodeposition on Pt electrode.

Acknowledgement

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