JOURNAL OF MARINE SCIENCES & ENVIRONMENTAL TECHNOLOGIES
Vol. 7, Issue No. 2 (December-2021)

ISSN (Print): 2413-5267
ISSN (Online): 2706-9966

LB Films of Octadecanoyl Hydroxamic Acid as Barrier against Copper Corrosion

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طبقات لانقمير وبلوجت من حمض الاوكتاديكانويل أحادي الهيدروكسيد كمانع ضد تآكل النحاس

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Received: 08 November 2021; Revised: 30 November 2021; Accepted: 05 December 2021.

Abstract

Free of ions of Octadecanoyl monohydroxamic acid ($C_{18}N$) and in the presence of Fe^{3+} ion multilayers were deposited on the copper surface as Langmuir-Blodgett (LB) films. Their inhibiting effect on copper corrosion was investigated in 0.1 M sodium sulfate solution by different techniques such as potentiodynamic polarization and by electrochemical impedance spectroscopy (EIS). As well as that, the copper surfaces were visualized using a Scanning electron microscope (SEM). The results showed that the highest inhibition efficiency (92%) was achieved by LB film of 5 monomolecular layers of $C_{18}N/Fe^{3+}$. The LB films work as a cathodic inhibitor which inhibits the cathodic reaction.

The presence of Fe^{3+} ions significantly improves the inhibition efficiency through the formation of a more compact dense layer of $C_{18}N/Fe^{3+}$ complex that blocks the flux of aggressive ions to the metal surface. The effect of immersion time on the inhibiting characteristics of LB films on the copper surfaces was studied.

***Keywords**: Monohydroxamic acid, LB films, Copper, Corrosion, EIS.*

الملخص

تم تغطية سطح نحاسي بعدة طبقات على شكل طبقات لانقمير وبلوجت من احماض الاوكتاديكانويل أحادي هيدروكسيد ($C_{18}N$) في وجود وفي عدم وجود ايونات الحديد الثلاثية (Fe^{3+}). وقد تم دراسة تأثير هذه الطبقات كمانع لتآكل النحاس في محلول كبريتات الصوديوم ذو تركيز مولي 0.1 بواسطة عدد من التقنيات المختلفة مثل الاستقطاب الديناميكي القوي والتنظير الطيفي للمقاومة الكهروكيميائية (EIS). بالإضافة إلى ذلك، تم تصوير الأسطح النحاسية باستخدام المجهر الإلكتروني للمسح الضوئي (SEM). وقد أظهرت النتائج أن أعلى كفاءة تثبيط (92٪) تحققت من خلال فيلم لانقمير وبلوجت من 5 طبقات أحادية الجزيئية من الحمض في وجود أيونات الحديد. كما تم استنتاج أن هذه الطبقات تعمل كمثبط كاثودي والتي تمنع تفاعل القطب السالب.

وجود الأيونات يحسن بشكل كبير من كفاءة التثبيط من خلال تشكيل طبقة كثيفة أكثر إحكاماً والتي تمنع تدفق الأيونات العدوانية إلى السطح المعدني. كما تم دراسة تأثير وقت الغمر على الخصائص المثبطة لأفلام لانقمير وبلوجت على سطح النحاس.

الكلمات الدالة: حمض أحادي هيدروكسيد، أفلام لانغمير وبلوجت، النحاس، التآكل، EIS.

1. Introduction

Copper, a relatively noble metal is important in the chemical and microelectronic industries due to its high thermal and electrical conductivity. However, a disadvantage in the use of copper is that it corrodes in acidic and strong alkaline solutions, especially in the presence of oxygen or oxidants. Corrosion inhibitors added in small concentrations to an aggressive environment are able to decrease corrosion processes. Compounds containing nitrogen, sulfur and oxygen, were often used as corrosion inhibitors of copper in different environments (Kaesche & Hackerman, 1958; Blomgren & Bockris, 1959; Bregman, 1963; Notoya, 1978; Garnese, 1987; and Stupnisek-Lisac & Gasparac, 2000; and Stupnišek-Lisac *et al*., 2002), such as benzotriazole (Gonzalez *et al*., 1993; Huynh *et al*., 2002; and Bellakhal & Dachraoui, 2004), conducting polymers (Ulman, 1991; Wolpers *et al*., 1992; Jaiswal *et al*., 1999; and Patil *et al*., 2004), and benzohydroxamic acids (Shaban *et al*., 1998). If these inhibitors are pre-adsorbed onto the metal surface in the form of well-organized molecular layer of controllable thickness, then one can expect better prevention in corrosive environment.

The Langmuir–Blodgett (LB) technique is one of the best techniques which produce very thin films (one or more monolayers) of ordered structures with controllable thickness at molecular level. Corrosion inhibition by LB films requires fewer chemicals for corrosion inhibition. The inhibitor film and their thickness can be regulated (Guo *et al*., 1994; and Meucci *et al*., 1999). Application of LB layers has environmental importance, and can be considered, as alternative to traditional techniques (chemicals used in coating at µm thickness) and thereby decreases the synthetic chemical burden on the environment. Functionalization of copper by different amphiphiles, mainly by thiols and mercapto derivatives (Volmer *et al*., 1990; Volmer *et al*., 1991; Laibinis & Whitesides, 1992; Yamamoto *et al*., 1993; Itoh *et al*., 1994; Jennings & Laibinis, 1996; Nozawa *et al*., 1997; and Grundmeier *et al*., 1998) resulted in corrosion-resistant surfaces by blocking the active sites of the metals. The effectiveness of corrosion inhibition by LB nanolayers depends on the structure of amphiphiles, on the chemical bonds at the interface between the metal surface and the layer, and on the composition of the layer. The protection efficiency of nanolayers is also influenced by the compactness and thickness of the nanofilm which is regulated by the number of layers (Xing *et al*., 1995; and Jaiswal *et al*., 2001).

The inhibition of copper corrosion by hydroxamic acid nanolayers developed on water subphase at different pH values was previously presented (Telegdi *et al*., 2004; Románszki *et al*., 2014; Zhu *et al*., 2017; and Luka Noč *et al*., 2021). At the air/water interface, the monolayers of hydroxamic acid on subphases with some divalent cations as well as their LB films on copper surface were also studied (Telegdi *et al*., 2005a & b; Al-Taher *et al*., 2005; Al-Taher *et al*., 2007; and Al-Taher *et al*., 2008). In the present work we demonstrate by electrochemical techniques the anticorrosion properties of ferric hydroxamate LB films deposited onto copper surface. SEM measurements were used to visualize the morphology of coated copper before and after immersion in corrosive solution.

2. Experimental Work

2.1. Materials

Octadecanoyl monohydroxamic acid [$CH_3(CH_2)_{16}CONHOH$, abbreviated as ($C_{18}N$)] (Structural formula is shown in Figure 1) was synthesized from stearoyl chloride and hydroxylamine in the presence of sodium hydrocarbonate. The purity was characterized by melting point, elemental analysis, infrared spectroscopy and thin layer chromatography. 6.5 mg of $C_{18}N$ dissolved in 10 mL of chloroform (Chemolab, Hungary) was the stock solution. Ultra-pure water (MilliQ system, 18.2 MΩ/cm) and an aqueous solution of $FeCl_3$ (5×10^{-5} M) was used as a subphase at certain pH values. The pH was adjusted to the desired value by adding dilute solutions of NaOH or HCl.

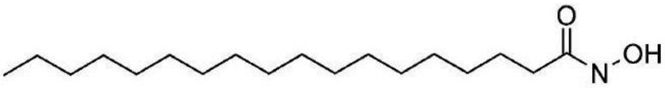

Figure 1. Structural formula of octadecanoyl hydroxamic Acid ($C_{18}N$)

The copper electrodes (99.99%) were shielded with epoxy resin except for the front face with an area of about 1.45 cm^2. The copper surfaces were polished first with SiC paper and then with diamond paste to a finish of 0.25 μm, and then washed by water and acetone in an ultrasound bath.

2.2. LB film preparation

An appropriate amount of the stock solution was spread onto the aqueous subphase in a Langmuir trough (NIMA Technology Ltd, 611D) by microsyringe. After complete evaporation of the solvent, compression was started at a speed of 100 cm^2/min to the target pressure. The surface pressure was measured by the Wihelmy plate method using filter paper. At a constant surface pressure of 35 mN/m where the monolayer has a so-called crystal structure (solid phase), LB nanolayes were deposited onto a copper electrodes with vertical deposition at the dipping speed of 10 mm/min.

The important measure of how efficiently a film was transferred onto a substrate is the transfer ratio (TR) which is defined as the area of monolayer removed from the subphase at constant pressure divided by the surface area of the dipped substrate. Theoretically, TR is one, if one molecular layer of the surface film is transferred onto the substrate surface with the same packing density. However, such transfer ratios are not often observed unless working with completely water insoluble compounds and substrates that are smooth on atomic scale.

2.3. Electrochemical measurements

A three-electrode electrochemical cell was used for electrochemical measurements. The working electrode was copper with and without LB nanolayers. A platinum plate and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. Polarization curves were measured using a potentiostat (Radiometer PGP-201) in aerated 0.1 M Na_2SO_4 solution at pH 3 with the scan rate of 10 mV/s. Electrochemical impedance spectroscopic measurements were performed using the Zahner Elektrik Impedance Measuring System (IM5d). Impedance spectra were obtained in the frequency range of 10 kHz to 10 mHz with perturbation amplitude of 10 mV. All electrochemical measurements were carried out at room temperature and all potentials were referred to the saturated calomel electrode (SCE).

2.4. Surface analytical technique

The morphology of the samples before and after immersion in corrosive solution was investigated by scanning electron microscopy (HITACHI S570), equipped with an energy dispersive X-ray spectrometer (RONTEC, EDR288) for chemical analysis. The SEM was operated by commercial RONTEC software.

3. Results and Discussion

3.1. Fabrication of LB films on copper surface

The surface pressure-molecular area isotherms (π-A) of hydroxamic acid monolayers on pure water surface and on aqueous Fe^{3+} subphases are shown in Figure (2). It is clear that the isotherm of monolayers on Fe^{3+} subphase is shifted into the more condensed phase than on ultrapure water surface that indicates the importance of Fe^{3+} ions dissolved in the subphase. This metal ion affects the behavior and compactness of monolayer. The molecular area in the monolayers at maximum compression decreased from 23 Å^2/molecule on pure water to about 21 Å^2/molecule on aqueous Fe^{3+} subphase.

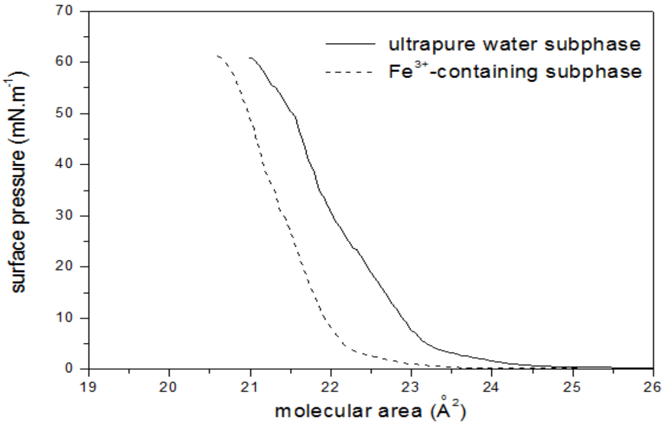

Figure 2. Pressure-area isotherm of $C_{18}N$ monolayers on pure water and Fe^{3+}-containing sub-phases at pH= 5.6.

The stability of $C_{18}N$ monolayers on aqueous Fe^{3+} subphase was tested by monitoring the change of molecular area as a function of time at certain surface pressure. The monolayer was compressed to the target pressure (35 mN/m) and held at compressed state, during that the change of molecular area as a function of time was registered. The result presented in Figure

(3), shows that the reduction of area in time was small, and therefore the monolayer was stable and could be transferred onto solid surfaces with high quality LB films.

During the multilayer deposition process, the observed transfer ratios (TR) for the studied LB films were around one with small deviation. In spite of this deviation in the TR, the total TR indicated that the nanolayers were well deposited onto the solid surface.

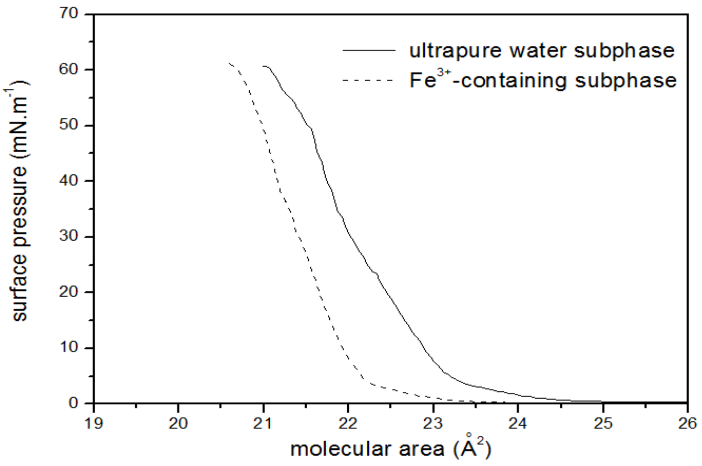

Figure 3. Stability of $C_{18}N$ monolayers on pure water and Fe^{3+}-containing sub-phases

3.2. Open circuit potential (OCP) measurements

The corrosion inhibition properties of the LB films on copper electrodes were studied by immersion tests in corrosive solution. The OCP as a function of time were recorded for bare and modified electrodes and presented in Figure (4). The OCP of the untreated electrode starts at -26 mV and after 5 hours of immersion time it reaches a value of -24 mV. The modification of the electrode with $C_{18}N$ LB film results in a shift of the OCP into negative value to around -40 mV, whereas, the presence of $C_{18}N/Fe^{3+}$ LB layers shift the OCP to more negative value up to -62 mV. These results show that both type of LB films, $C_{18}N$ and $C_{18}N/Fe^{3+}$, can inhibit the cathodic process in the copper corrosion. After 10 hours the OCP values are similar to that of the unmodified copper electrode. This is most likely due to the process, defect places and damages in the LB films and the result is that the aggressive components can reach the metal surface decreasing efficiency.

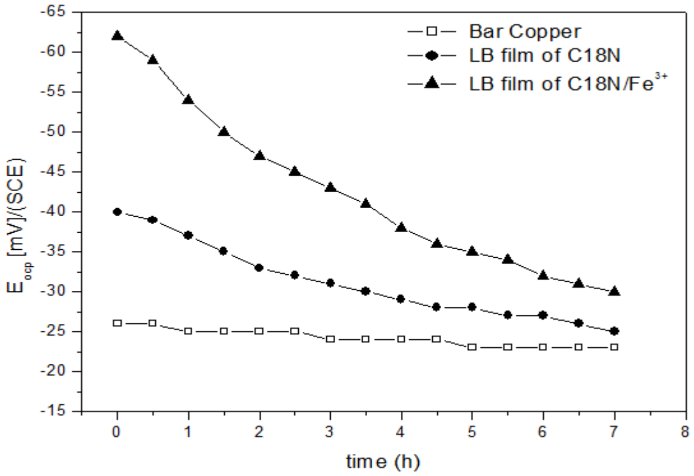

Figure 4. OCP measurements on copper electrodes vs. time in 0.1 M Na_2SO_4 solution (pH 3)

3.3. Polarization measurements

The potentiodynamic polarization curves for uncoated and coated copper with LB films of $C_{18}N$ and $C_{18}N/Fe^{3+}$ in 0.1 M Na_2SO_4 solution are shown in Figure (5). The corrosion kinetic parameters and inhibition efficiencies are given in Table (1). The inhibition efficiency was calculated according to Eqn. (1) (Bregman, 1963):

$$\eta = \frac{i_{corr} - i_{corr(coated)}}{i_{corr}} \% \qquad \ldots\ldots \quad (1)$$

where i_{corr} and $i_{corr\ (coated)}$ are the corrosion current density values without and with LB film, respectively, determined by Tafel extrapolation to the corrosion potential.

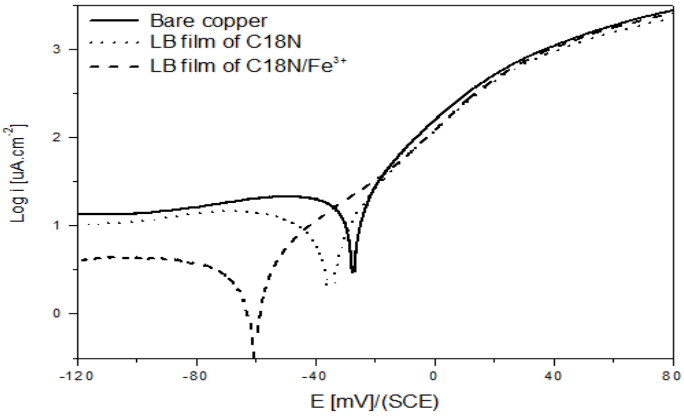

Figure 5. Polarization curves measured on copper electrodes with and without 5 LB monomolecular layers in 0.1 M Na_2SO_4 solution, pH 3 (scan rate 10 mV/min)

In the case of copper modified with $C_{18}N$ LB film, the corrosion potential (E_{corr}) is shifted to a negative value (-35 mV), with moderate inhibition efficiency about 70%. Whereas, the presence of $C_{18}N/Fe^{3+}$ LB layers results in a more negative shift of the E_{corr} (to

-60 mV) if one compare this value with that one measured without any coating (-24 mV), and in a significant increase in anticorrosion efficiency (92%). In both type of LB layers, the cathodic reactions of copper are inhibited.

Table 1. Corrosion potential (E_{corr}), corrosion current densities (i_{corr}), and inhibition efficiencies (η) of copper electrodes modified with 5 LB monomolecular layers.

Copper electrodes	E_{corr} (mV)	i_{corr} ($\mu A.cm^{-2}$)	η(%)
Bare (without modification)	-27	7.2	--
Modified with LB film of $C_{18}N$	-35	2.1	71
Modified with LB film of $C_{18}N/Fe^{3+}$	-60	0.56	92

The cathodic current density significantly decreases, most likely due to the formation of a homogeneous insoluble stable complex of C_{18}/Fe^{3+} on the copper surface, which would control the cathodic reactions.

3.4. EIS measurements

Impedance spectra of the unmodified and modified copper with LB films in 0.1 M Na_2SO_4 solution are shown in Figure (6). The charge transfer resistance value (R_p) derived from impedance spectra and calculated efficiency are given in Table (2). One capacitive loop appears in the spectrum of modified copper with LB films. The presence of a single semicircle depicts a single charge-transfer process during corrosion processes. As shown in Figure (6), the LB film of $C_{18}N/Fe^{3+}$ produces better inhibiting efficiency than the $C_{18}N$ LB film. These results support those one got by polarization measurements. After two hour immersion in sulfate solution, the inhibition efficiency of $C_{18}N/Fe^{3+}$ LB film is still much higher than that of the $C_{18}N$ LB film. This proves the stability and effectiveness of the $C_{18}N/Fe^{3+}$ complex on copper. However, the inhibition efficiencies for both LB films decrease with increasing immersion time. This is due to the penetration of aggressive ions from the electrolyte into the nanolayers which causes defects in the films.

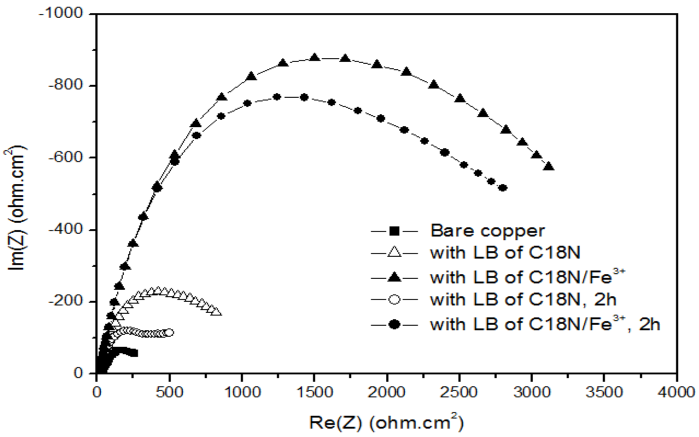

Figure 6. Nyquist plot of EIS measurements on copper electrodes with and without 5 LB monomolecular layers in 0.1 M Na_2SO_4 solution (pH 3)

Table 2: Polarization resistance values (R_p) and calculated inhibition efficiencies (η) of LB modified copper electrodes.

Copper electrodes	R_p ($\Omega.cm^{-2}$)	η(%)
Bare (without modification)	311	--
Modified with LB film of $C_{18}N$	1046	70
Modified with LB film of $C_{18}N/Fe^{3+}$	3873	92

3.5. Morphological studies

The surface morphology of a bare and LB-film modified copper specimens was studied by scanning electron microscopy (SEM). The images in Figure (7) show the morphology of the bare and LB-film modified copper specimens, the photographs were taken before and after immersion of specimens in 0.1 M Na_2SO_4 (pH 3) for 2 hrs. Figures (7a-c) represent the bare copper, the modified copper with $C_{18}N$ LB film, and $C_{18}N/Fe^{3+}$ LB film, respectively, before exposure to corrosive media. Figures (7d-f) show the photographs of bare copper and modified coppers after immersion into the corrosive solution. These figures present clearly that the copper covered by $C_{18}N/Fe^{3+}$ LB film suffers from less corrosion attack than the bare copper and even less than that one which was modified with $C_{18}N$ LB film. These images also prove that the $C_{18}N/Fe^{3+}$ LB film efficiently inhibits the copper corrosion in acidic sodium sulfate. These observations are in agreement with the electrochemical results.

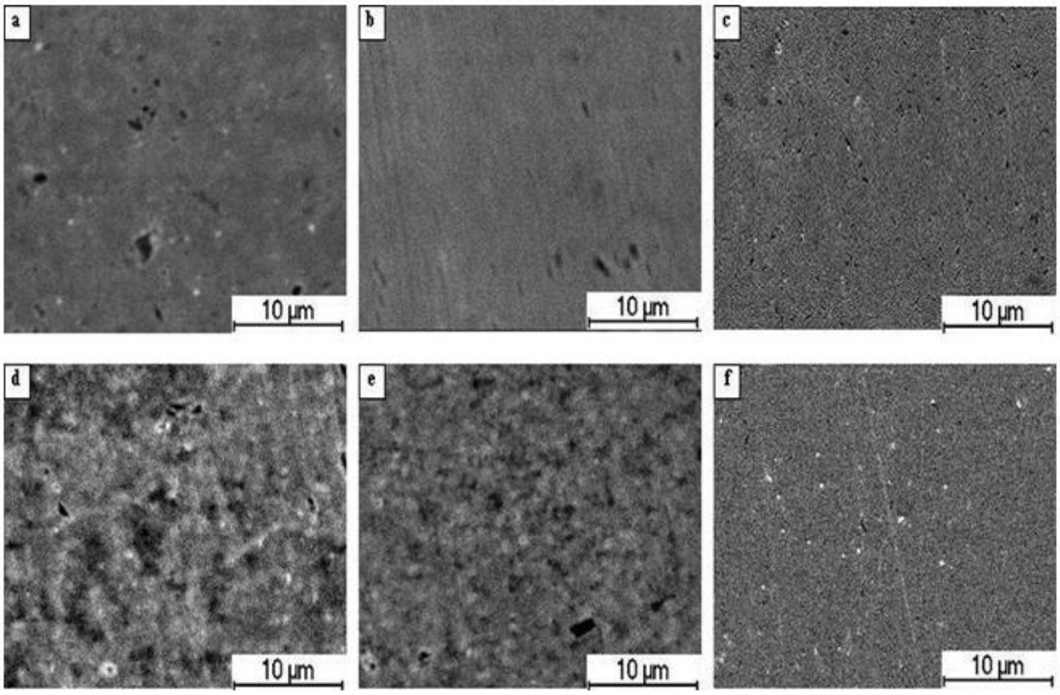

Figure 7. SEM images of copper surface before and after corrosion experiments, copper surface without modification (a and d); copper surface modified with $C_{18}N$ (b and e); and copper surface modified with $C_{18}N/Fe^{3+}$ (c and f).

4. Conclusion

- The deposited LB nanolayers of $C_{18}N/Fe^{3+}$ onto copper surface showed good stability and anti-corrosion activity in acidic aqueous solution.
- The multilayers of $C_{18}N/Fe^{3+}$ inhibited the copper corrosion efficiently, a 92% of inhibition efficiency was achieved.
- The inhibition mechanism could be atributed to the blocking action of LB films on the surface throughout formation of compact, dense layer of $C_{18}N/Fe^{3+}$ complex.
- The inhibition efficiencies for both LB films decrease with increasing immersion time which could be due to the defects in the nanolayers which allows the transfer of aggressive ions through the film.

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