



Template-assisted Electrodeposition of Freestanding Sn, In and Sn-In Nanowire Arrays in an Ionic Liquid



S.A. Al Kiey¹, A.A. El-Warraky¹, S.S. Abdel Rehim², S. Zein El Abedin^{1*}

¹Physical Chemistry Department, Electrochemistry and Corrosion lab., National Research Centre, 33-El-Behouth St., Dokki, Cairo, Egypt.

²Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt.

IN this paper we report on the template assisted electrochemical synthesis of Sn, In, and Sn-In nanowire arrays in the air and water stable ionic liquid 1-ethyl-3-methylimidazolium trifluoromethylsulfonate ([EMIm]TfO). Polycarbonate membrane was employed as a template for the synthesis of nanowires. The electrochemical synthesis of nanowire arrays occurred in two steps; the electrodeposition inside the pores of the membrane and the chemical dissolution of the membrane. The results show that high quality, freestanding nanowire arrays of Sn, In and Sn-In, can be made in the employed ionic liquid electrolytes via a template-assisted electrodeposition regime. The reported synthesis process is quite facile and assures the formation of mechanically stable, freestanding nanowire arrays.

Keywords: Ionic liquid, Electrodeposition, Tin, indium, Template-assisted.

Introduction

Tin and tin based alloys are regarded as potential candidates for the application as anodes in lithium ion batteries [1-5]. The high theoretical capacity of tin (991 mA h/g [6], compared with that of the traditional graphite (372 mA h/g [7], makes it a promising anode material for the future generation of Li-ion batteries. However, the major drawback in employing metallic anodes, in general, is the large volume expansion and the subsequent pulverization that occurs during cyclic, leading to capacity fading [8-10]. It was reported that the three-dimensional structuring of the anodes can overcome the problems associated with the large volume changes on cycling [11]. It was shown that the 3D-nanowire electrodes can accommodate the volume expansion resulting from Li insertion/deinsertion during cycling [12-16].

In this paper we aim at the synthesis of 3D Sn, In, and Sn-In nanowire arrays via the template assisted electrodeposition approach

using an ionic liquid electrolyte. Indium is also an attractive anode candidate due to its high theoretical capacity (1012 mAh/g [17]. The ionic liquid 1-ethyl-3-methylimidazolium trifluoromethylsulfonate ([EMIm]TfO) was employed. SnCl₂ and InCl₃ were used as sources of Sn and In, respectively. It is worth noting that tin and indium can be electrodeposited using aqueous electrolytes [18-21]. However, aqueous electrolytes usually exhibit serious drawbacks including, the low current efficiency, the dendritic growth of the deposits, and hydrogen evolution during deposition [22]. Furthermore, the massive hydrolysis of the precursors in aqueous solutions and the consecutive formation of metal hydroxides negatively influence the electrodeposition process [23].

Most of the drawbacks of using aqueous electrolytes for electrodeposition of tin can be avoided using ionic liquid electrolytes [24-26]. The electrodeposition of tin and indium-tin alloy

*Corresponding author e-mail: sherifzein888@yahoo.com

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from the ionic liquid [EMIm]BF₄/[EMIm]Cl was reported [27,28]. Porous tin was electrodeposited from dicyanamide based ionic liquids [29]. Recently, we showed the electrodeposition of Sn films from the ionic liquid [EMIm]TfO under ambient atmosphere [30]. The electrodeposition of indium from ionic liquid electrolytes was also reported [31,32].

We show in this paper that freestanding, stable nanowire arrays of Sn, In, and Sn-In, can be made in the employed ionic liquid. The obtained nanowire arrays are made on an electrodeposited copper supporting layer. The Cu-layer keeps the nanowires freestanding and prevents the nanowire structure from collapsing.

Experimental

The electrodeposition of nanowire films of Sn, In and Sn-In alloy was investigated in the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethylsulfonate with high purity (IOLITEC, Germany). The ionic liquid was used as received without further purification or drying. SnCl₂ (Alfa Aesar, 99.99 %) and InCl₃ (MERCK, 99.99 %) were used as sources of tin and indium, respectively. The concentration of SnCl₂ and InCl₃ in the employed ionic liquid was 0.1M.

Track-etched polycarbonate (PC) membranes (Ion Track Technology for Innovative Products, IT4IP, Belgium) were used as templates for the electrochemical synthesis of nanowires. The membrane was sputtered by a very thin film of gold, about 30 nm thick, to make it conductive and serve as working electrode. Dichloromethane was employed to dissolve the polycarbonate membranes. Pt wires (Alfa, 99.99 %) were used as quasi-reference and counter electrodes. A copper supporting layer was electrodeposited on the gold sputtered side of the membrane using an acidic CuSO₄ bath under potentiostatic conditions.

The electrochemical measurements were conducted using a Verstat 263A Potentiostat/Galvanostat (Princeton Applied Research). The experiments were performed under air and at ambient temperature. The nanowire films were investigated by a high resolution field emission scanning electron microscope (FEG 250) with energy dispersive X-ray analysis.

Results and Discussion

Cyclic voltammetry

The cyclic voltammetry behaviour of the employed ionic liquid containing tin and indium precursors was investigated. Figure *Egypt.J.Chem.* **62**, No. 4 (2019)

1 shows the cyclic voltammograms of 0.1 M SnCl₂/ [EMIm]TfO, 0.1M InCl₃/[EMIm]TfO and of the mixture 0.1 M SnCl₂ + 0.1 M InCl₃/ [EMIm]TfO, recorded on the gold sputtered PC membrane. Initially, the electrode potential was ramped down from the open circuit potential (-0.08 V, -0.05 V and +0.01 V (vs. Pt) for SnCl₂, InCl₃ and SnCl₂/InCl₃ electrolytes, respectively) in the negative direction with a scan rate of 10 mV/s up to a potential of -2.0 V (vs. Pt). Then the potential was scanned back in the anodic direction up to a potential of 0.2 V (vs. Pt) and finally terminated at the open circuit potential. The CV of 0.1 M SnCl₂/[EMIm]TfO shows two cathodic peaks c₁ and c₂ in the forward scan with their anodic counterparts in the backward scan. The reduction peak at c₁ might be ascribed to the alloying of Sn with Au and the reduction peak at c₂ is due to the bulk deposition of Sn. Similar cyclic voltammetry behaviour of the employed ionic liquid electrolyte was shown in ref. [31].

The cyclic voltammogram of 0.1M InCl₃/ [EMIm]TfO, recorded on the Au-sputtered side of the PC membrane, displays two distinct cathodic processes in the forward scan with their anodic counterparts in the backward scan. The first process can be correlated to In alloying with Au and the second process is ascribed to the bulk deposition of In. Similar features of the recorded cyclic voltammogram was shown in ref. [32]. The cathodic branch of the cyclic voltammogram of the ionic liquid [EMIm]TfO containing 0.1 M SnCl₂ and 0.1 M InCl₃ shows two cathodic waves (c₁ and c₂) and a pronounced cathodic peak (c₃). The first two cathodic processes might be attributable to Sn-Au alloying and bulk deposition of Sn, respectively. The cathodic peak c₃ is obviously due to the Sn-In codeposition. On the anodic branch of the cyclic voltammogram, two pronounced anodic processes were observed. The anodic process a₂ is correlated to the stripping of Sn-In deposits. The wide anodic process a₁ can be ascribed to the oxidation of the deposited Sn and surface alloy film of Sn-Au.

Electrodeposition of nanowire films of Sn, In and Sn-In

The template-assisted electrochemical synthesis of Sn, In and Sn-In nanowire arrays was performed in the ionic liquid [EMIm] TfO using polycarbonate templates. Generally,

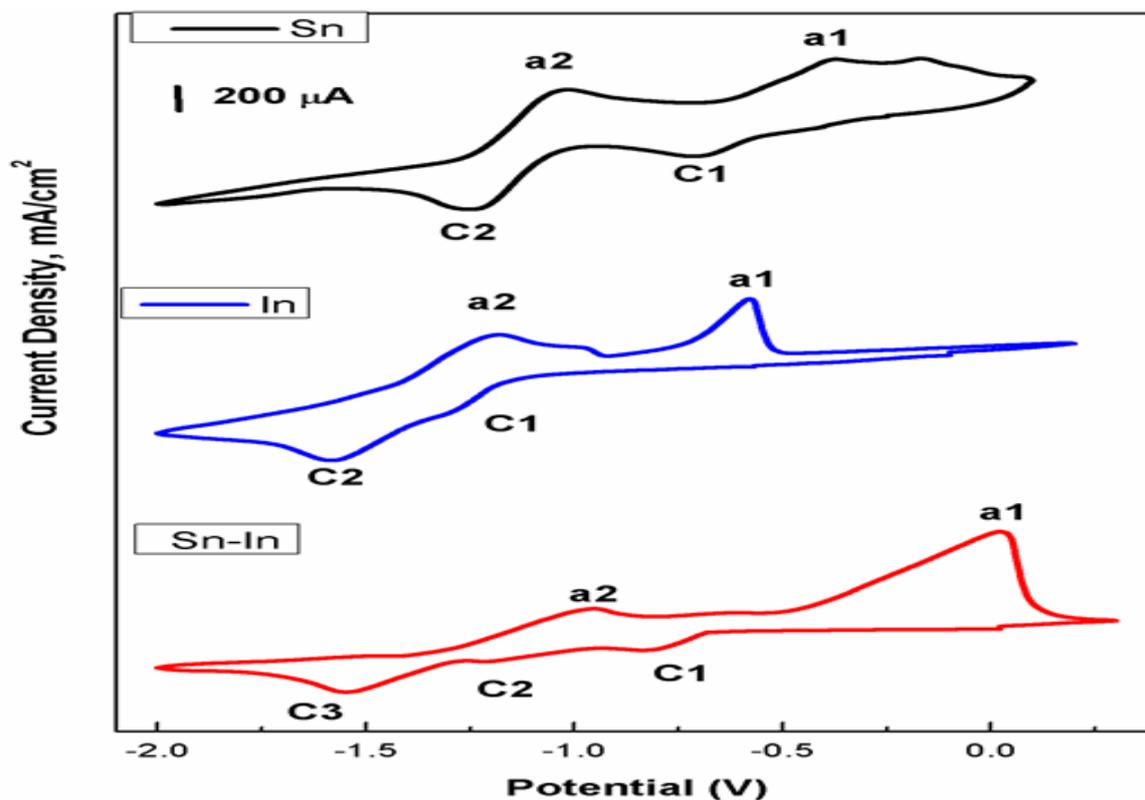


Fig. 1. Cyclic voltammograms of 0.1 M SnCl_2 , 0.1 M InCl_3 and 0.1 M $\text{SnCl}_2 + 0.1 \text{ M InCl}_3$ in the ionic liquid [EMIm]TfO with a scan rate of 10 mV/s at room temperature.

the utilization of templates has the advantage of getting nanowires with pre-defined and controllable sizes and shapes in addition to the possibility to form vertically aligned nanowire arrays. Prior to the electrodeposition of the nanowires, copper supporting layers were electrodeposited on the gold sputtered side of the PC membrane. Then, nanowires were deposited in a different step within the pores of the non-sputtered side of the membrane. After the chemical dissolution of the PC membrane in dichloromethane, freestanding nanowire structures on an electrodeposited Cu supporting layer were obtained.

Figure 2a shows SEM micrograph of Sn nanowire arrays obtained potentiostatically from the ionic liquid electrolyte 0.1 M SnCl_2 /[EMIm]TfO at a potential of -1.3 V (vs. Pt) for 1 h. As seen, freestanding Sn nanowires with a homogenous length of about 5 μm were obtained. The Sn nanowires are densely indicating the complete wetting pores of the membrane by the ionic liquid electrolyte which, in turn, leads to homogenous deposition inside the pores and the formation of dense nanowires. The accompanied EDX profile,

Fig. 2b, of the Sn nanowire film reveals the purity of the obtained nanowires as only Sn, Cu and Au were recorded. Au and Cu were detected from the sputtered Au film and the electrodeposited Cu supporting layer, respectively.

Figure 3 shows SEM micrograph of In nanowire film obtained from the ionic liquid electrolyte 0.1 M InCl_3 /[EMIm]TfO at a potential of -1.7 V (vs. Pt) for 1 h. As seen, freestanding In nanowire arrays are obtained with homogenous lengths of about 5 μm . The EDX profile of the obtained In nanowires reveals the purity of the electrodeposited In nanowires.

The potentiostatic electrodeposition of Sn-In nanowire arrays was also performed in the ionic liquid [EMIm]TfO containing 0.1 M SnCl_2 and 0.1 M InCl_3 at a potential of -1.7 V (vs. Pt) for 1 h. Figure 4a shows SEM micrographs of the obtained Sn-In nanowire film. As shown in the SEM micrograph of Fig. 4a, vertically aligned nanowire bunches of Sn-In were obtained. The nanowires are connected together from the tops forming bunches. The EDX profile of the

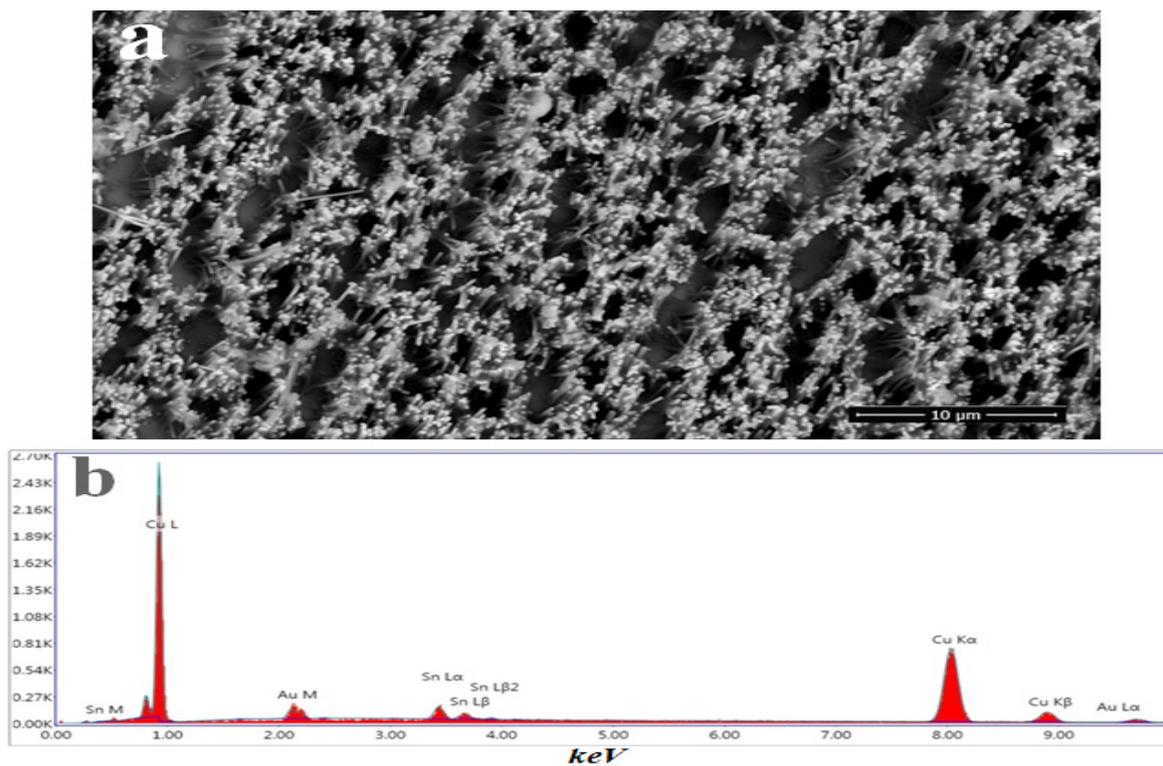


Fig.2. SEM micrograph (a) and EDX spectrum (b) of freestanding Sn nanowires obtained from 0.1 M SnCl_2 /[EMIm]TfO solutions by electrodeposition at a potential of -1.3 V vs. Pt for 1 h.

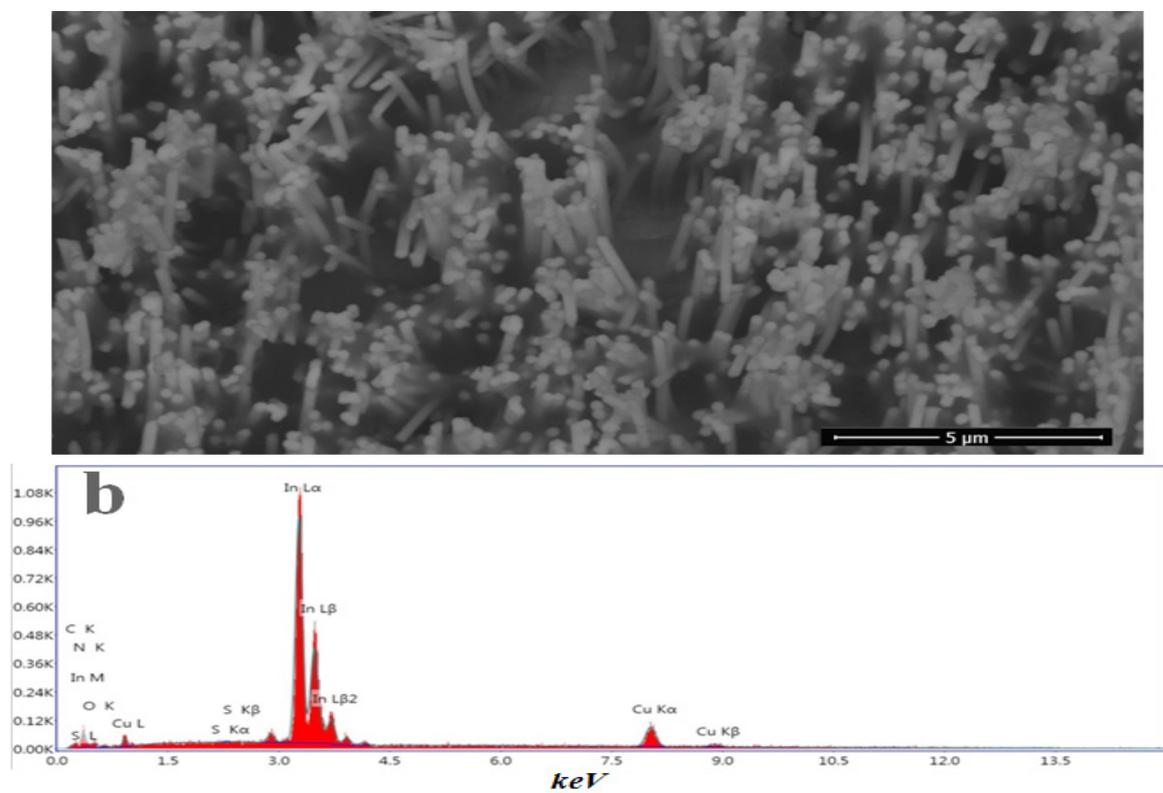


Fig. 3. SEM micrograph (a) and EDX spectrum (b) of freestanding In nanowires obtained from 0.1 M InCl_3 /[EMIm]TfO solutions by electrodeposition at a potential of -1.7 V vs. Pt for 1 h.

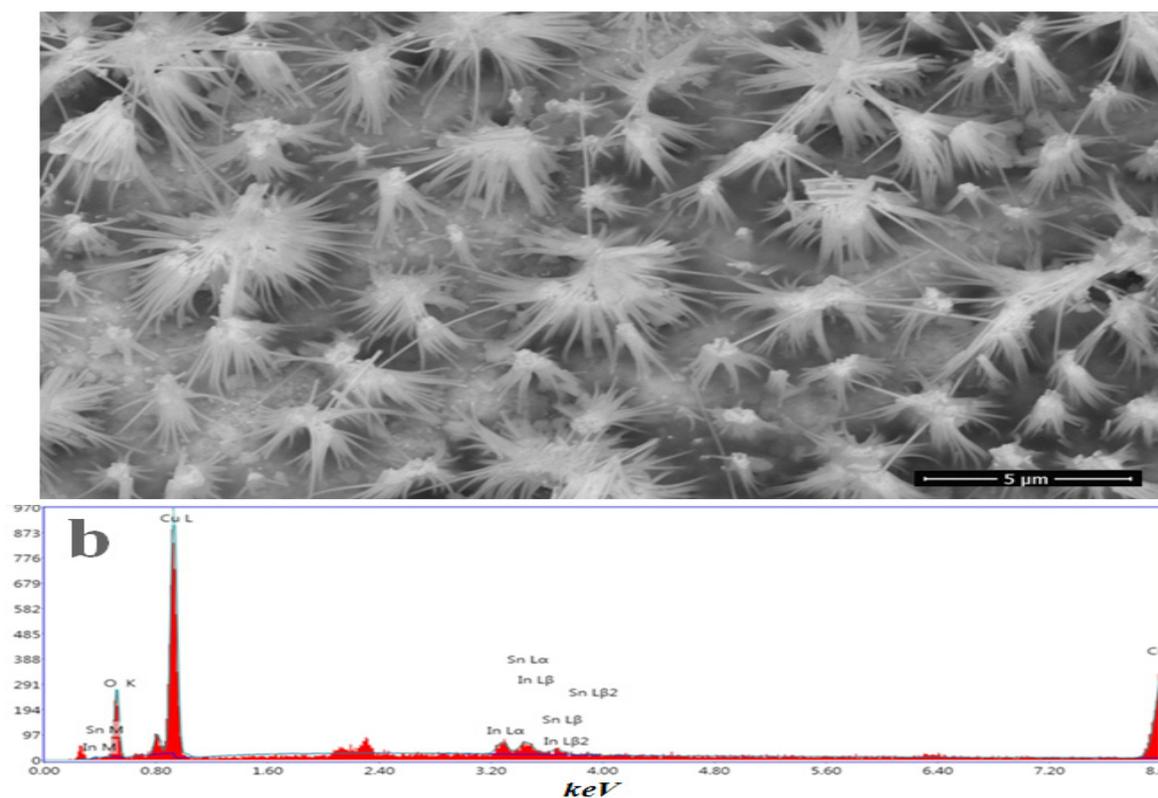


Fig. 4. SEM micrograph (a) and EDX spectrum (b) of Sn-In nanowires obtained from 0.1M SnCl_2 + 0.1 M InCl_3 / [EMIm]TfO solutions by electrodeposition at a potential of -1.7 V vs. Pt for 1 h.

obtained Sn-In shows the characteristic peaks of both Sn and In indicating the electrodeposition of Sn-In nanowire film (Fig. 4b).

Such nanowire structures are highly interesting for the application as anodes in Li ion batteries as the free space between the wires makes the diffusion of Li ion into the nanowire film easier and also the large volume change, which occurs during cycling, can be easily accommodated. This would lead to a better anode performance [11, 16].

Conclusions

The electrochemical synthesis of freestanding, stable nanowire arrays of Sn, In and Sn-In in the ionic liquid [EMIm]TfO via a template-assisted approach was showed. The results showed that high quality nanowire arrays of Sn, In and Sn-In can be electrochemically obtained. The nanowire arrays were mechanically supported by an electrodeposited Cu film formed on the back side of the PC membrane prior to deposition of the nanowires. This would lead to a significant improvement in the performance of the obtained

nanowire films when they are employed as anodes in Li-ion batteries.

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الترسيب الكهربى لمصفوفات اسلاك نانويه من Sn , In , Sn-In في سائل أيوني باستخدام قوالب مساعده

شريف القيعى¹، على الوراقى¹، سيد ثابت عبد الرحيم²، شريف زين العابدين¹
¹قسم الكيمياء الفيزيقيه – المركز القومى للبحوث – الدقى – الجيزه - مصر.
²قسم الكيمياء – كلية العلوم – جامعة عين شمس – العباسيه - القاهره - مصر.

يتناول هذا البحث تحضير مصفوفات الأسلاك النانوية من Sn, In و Sn-In في السائل الأيونى [EMIm]TfO وقد تم استخدام غشاء بولى كربونات كقالب لتحضير الأسلاك النانوية بالترسيب الكهربى بداخل ثقوب الغشاء. وقد تم التحضير الكهروكيميائى لمصفوفات الأسلاك المتناهية فى الصغر فى خطوتى اساسيتين وهما: الترسيب الكهربى داخل مسام الغشاء ثم التخلص من الغشاء عن طريق الذوبان الكيميائى فى المذيب العضوى ثنائى كلوريد الميثان. وقد اظهرت النتائج امكانية تحضير مصفوفات أسلاك نانويه قائمه بذاتها وبجوده عاليه من Sn-In، In، Sn فى السائل الايونى المستخدم بطريقة الترسيب الكهربى بمساعدة اغشية البولى كربونات. وتتميز طريقة التحضير ببساطتها وايضا تكون مصفوفات الاسلاك المحضره بانها قائمه بذاتها وذات ثبات ميكانيكى عالى.