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PREPARATION AND CHARACTERIZATION OF IRON THIN FILM ELECTRODEPOSED ON A VITREOUS CARBON ELECTRODE IN AQUEOUS AND ORGANIC MEDIA: A COMPARATIVE STUDY

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Résumé

L'électrodéposition du fer, sous forme d'un mince film sur du carbone vitreux dans différents milieux aqueux et organiques, a été étudiée. Le dépôt de fer a été étudié par voltamétrie cyclique. La quantité de fer déposé a été déterminée par intégration des pics cathodique et anodique de Fe(0) et Fe(II) dans différents milieux.

Mots clés: Al fer, mince film, voltamétrie cyclique, électrodéposition

Abstract

The deposition by electrochemical way in the form of an iron thin film was studied on a vitreous carbon electrode in various aqueous and organic media. The deposit of iron was studied by cyclic voltammetry; the quantity of iron deposited was determined by integration of the cathodic and anodic peaks of Fe (0) and Fe (II) of the various media.

Keywords: iron, thin film, cyclic voltammetry, electrodeposition.

ملخص

ترسب كهروكيميائية على شكل طبقة رقيقة من الحديد على الكربون زجاجي في مختلف الأوساط المائية والعضوية تمت دراستها ترسب الحديد ما تمت دراسته من قبل فولطميتري دوري حددت كميت الحديد المترسبة بدمج قمم أنودية وكاتودي ل Fe (0) و Fe (II) في مختلف الأوساط

الكلمات المفتاحيـــــة : الحديد، طبقة رقيقة، فولطميتري دوري، ترسيب الكهربائي

INTRODUCTION

The electrolytic alloy or metal deposits are the subject of a private interest, in particular as regards to their use in industry in objectives of decoration of surface or protection of the materials [1,2]. The first studies related to the electrolytic deposit of iron alloys have been published during the period 1969 - 1970 [3, 4]. Recently, attention has been given to electrolytic deposits of pure iron film as a ferromagnetic component.

R. Krumm and B. Guel have studied for the third time, nucleation and the growth of the metal electrodeposition on NR If (111), whereas Darko Grujicic and Batric Pesic studied the reactions and the mechanisms of nucleation of the electrodeposition of copper [5]. Y. Yoo and S.C.Hernandez have also studied the electrodeposition of FeCoNi in the form of thin films for magnetic devices MEMS [6].

In the same way, Hirofumi Ebe, and Mikito Ueda have reported the electrodeposition of Sb, Bi, Te and their alloy [7]. E. Jartych and co-workers studied the film electrodeposition of $CuInSe_2$ for the application for the photovoltaic one [8]. Hanna Bryngelsson and Jonas Eskhult electro deposed coatings made up of nanoparticules of Sb and Sb_2S_3 being used as materials for the anode Li-ion. J. Zarpellon and H. F. Jurca have described the deposit of metal iron on If (1 1 1) by the method of electrodeposition in sulfate and a saccharin sodium solution of ammonium [9]. Recently, H. Matsushima and co-workers have studied the effects of the magnetic fields on the electrolytic iron deposit [10]. More recently, J. Zarpellon, H.F. Jurcaont carried out their experiments on the electrodeposition of iron [11]. Olivier Zaouak and co-workers have also deposited bismuth for the development of a microsensor screen prints [12].

The preparation of metal thin films of transition such as Ni, Co, Cu and Fe drew a considerable attention because of their potential applications in scientific disciplines and technological [13].

Moreover Gowand Hutton has studied the electro - deposition of a thin iron film [14]. More recently, several studies feel on the thin film electrodeposition of iron made by F. Lallemand [15-17].

The aim of this study is to develop a thin layer of iron deposits on a vitreous carbon electrode in different media. This electrode must be provided by electrochemical synthesis of complexes of Fe (II) as $LiFePO_4$.

1. EXPERIMENTAL

2.1 CHEMISTRY

The chemical reagents used were commercial products used without additional purification: sulphuric acid (96%), acetic acid (99%) and N, N-dimethylformamide were obtained from Fluka products; sodium hydroxide (97%), lithium hydrogenophosphate, lithium hydroxide ; ferrous chloride (97%) and sulfate of hexahydrate ferrous ammonia (extra Pure) were provided by Carlos Erba, Aldrich and Scharlau respectively.

2.2 ELECTROCHEMICAL STUDIES

The electrochemical studies were carried out using a potentiostat EGG Model 362 connected to a plotting table X-Y Kipp and Zonen, in a cell with three electrodes. The working electrode was a stationary or vitreous carbon disc turning 2 mm in diameter. The potentials were measured compared to a reference electrode of saturated calomel (ECS). The auxiliary electrode consisted on a graphite bar. The working electrode was cleaned after each measurement by polishing on abrasive papers of different granulometries. Deoxygenating was ensured by nitrogen splashing. All measurements were taken at room temperature. The quantities of current were determined by integration.

3. RESULTS AND DISCUSSION

3.1 VOLTAMMETRIC STUDIES IN AQUEOUS MEDIUM

The method consists of recording the voltammograms of iron cations in regime of stationary convective diffusion to an electrode stationary and rotating .Indeed, this method must make it possible to visualize the consequences which rise from the contacts that the ions with the electrode can have. In order to cover the field of the potentials available in aqueous medium, the voltammograms were recorded with scanning potential carried out initially towards the negative values then after inversion, the electrodeposed metal on the electrode, dissolves (fig.3). Tests have been carried out in various aqueous media such as the sulphuric acid, the ammonium acetate and the acetic acid. Among these various media it is the acetic acid which appeared the best to us.

3.1.1 BEHAVIOR OF FE^{2+}

The study of 5.10^{-3} $mol.L^{-1}$ Fe^{2+} concentration in 10^{-1} $mol.L^{-1}$ acetic acid and 10^{-1} $mol.L^{-1}$ sodium acetate media, shows that during scanning with 100 mV/S, between -1.4V/ECS and + 1.0 V/ECS, Fe (0) oxidizes at – 0.65 V/ECS and Fe (II) oxidizes at + 0.7 V/ECS. On the other hand, the Fe (III) reduction is to + 0.04 V/ECS and that of Fe (II) is in extreme cases of the cathodic current – 1.4 V/ECS (fig. 1).

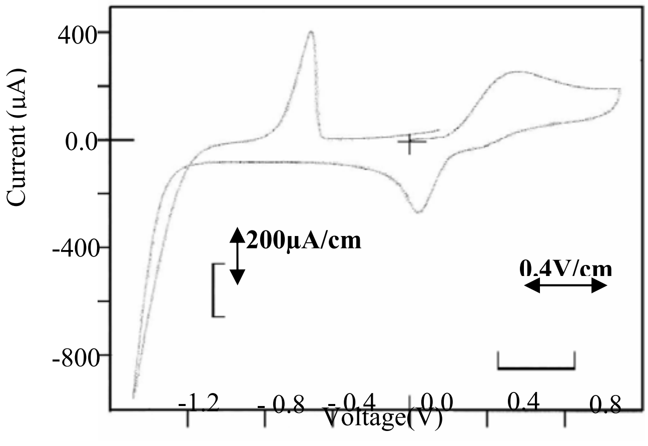

Fig.1: Cathodic current – 1.4 V/ECS

3.1.2 RESPONSE OF A MODIFIED VITREOUS CARBON MODIFIED ELECTRODE

The method consists in, first of all, preparing an iron electrode on vitreous carbon (V.C) by electrodeposition of an iron film starting from an acetic solution containing a ferrous salt. The formed electrode is then plunged in an acetic solution deprived of iron ions. Deposition voltammograms of iron film and its dissolution) were recorded (fig.2 and fig.3). The decrease on current density, observed on the voltammograms of anodic dissolution repeated successively, clearly shows the electrodeposition of iron on vitreous carbon.

This voltammogram (fig. 2) corresponds to the following reactions:

$$Fe\ (II) + 2e^- \rightarrow Fe\ (0)$$

$$Fe\ (0) \rightarrow Fe\ (II) + 2e^-$$

The deposit of iron was studied on an electrode of vitreous carbon in a solution of composition CH_3CO_2H at 1.10^{-1}mol. L^{-1}, CH $_3CO_2Na$ at 1.10^{-1} mol.L^{-1}containing 5.10^{-3} mol. L^{-1} of $FeCl_2$, after deoxygenating the solution by nitrogen during ten minutes.

The electroactivity of iron on a stationary vitreous carbon electrode is represented on figure 2. The electrodeposition of iron begins to – 1.20 V/ECS and quickly reaches a stage of diffusion during the cathodic scanning of the potentials. The vitreous carbon electrode is covere by iron, while scanning back. The ferrous ions are reduced more easily on this iron cathode. Electrodeposed iron is oxidized while anodic scanning at – 0.3 V/ECS what appears by an anodic peak and a rapid decrease of the current until its cancellation (fig. 2). The electrode obtained is an iron electrode on vitreous carbon. The study reveals that during scanning with 10 mV/S between – 0.3 and – 1.4 V/ECS a voltammogram presenting a peak of Fe (0) deposit on the electrode of V.C at -1.4 V/ECS (fig. 2). This deposit is confirmed by the electrochemical study of the electrode in V.C modified in a solution of 1.10^{-1} mol.L^{-1} composition acetic acid 1.10^{-1} mol.L^{-1} of sodium acetate 1.10^{-1} mol.L^{-1} free from $FeCl_2$.

In order to dissolve iron, we carried out a scanning of potential of – 0.9 to + 1.0 V/ECS then with -1.4 V/ECS. The voltammogram comprised a peak of dissolution of Fe (0) (fig.3) quite symmetrical which appears with the potential – 0. 3 V/ECS followed by another peak more spread out to the potential + 0.12 V/ECS corresponding to Fe (II) oxidation out of Fe (III).

The many scannings carried out in return ticket from – 1.0 to + 1.0 V/ECS and a return to -1.4 V/ECS make it possible to note a decrease of the current until it becomes null (fig.3). After graphic integration in one notes that the report of the quantities of anode current and cathodic Qa/Qc is of 0.41 relatively far away from the theoretical value 1. The important variation compared to the theoretical value is not has a phenomenon of passivation which would block the oxidation of electrodeposed iron. This weak Qa/Qc could be explained, except error of integration, by a cathodic current of hydrogen formation partially confused with the Fe (II) reduction could be at the origin of an error of integration in the calculation of the quantities of electricity.

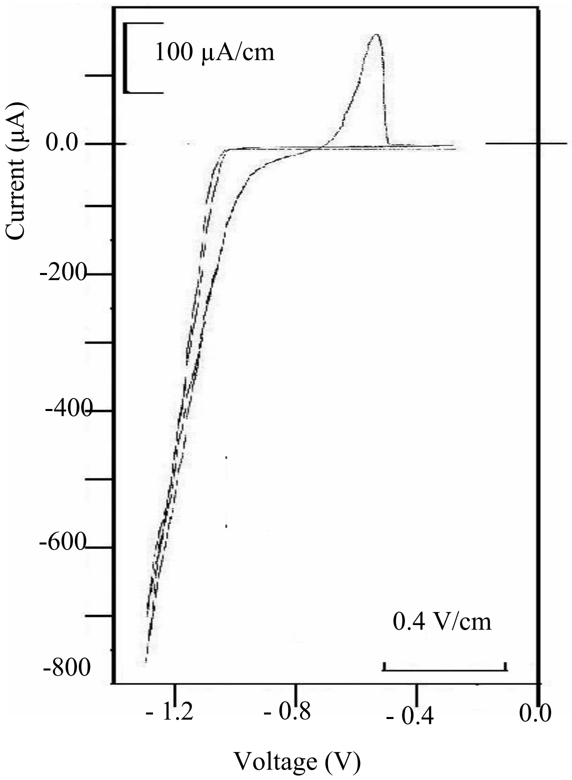

Fig. 2: Voltammogram of the Fe electrodeposition on an electrode out of V.C in a solution of 1.10^{-1} mol.L^{-1} acetic acid and 1.10^{-1}mol.L^{-1} sodium acetate containing 1.10^{-2} mol.L^{-1} of $FeCl_2$; stationary electrode out of V. C, (Ø = 4 mm, scanning rate: V = 10 mV.s^{-1}. Thickness of the iron deposit is of 23.78 µm.

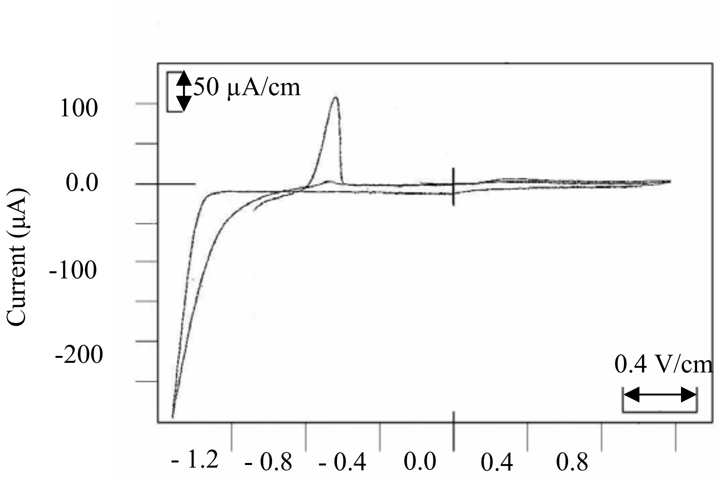

Fig. 3: Voltammogram of the dissolution of iron in a solution of composition: 1.10^{-1} mol. L^{-1} acetic acid and 1. 10^{-1} mol. L^{-1} sodium acetate; electrode out of V. C modified (Ø =4 mm, scanning rate of the potentials: V= 100 mV/S).

The deposit of iron formed on the electrode has quite precise potentials after scanning back

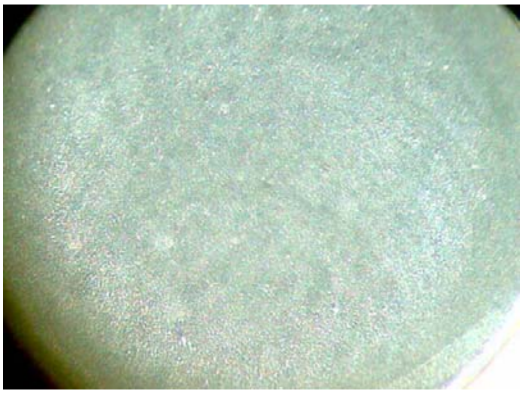

Image-1: Image of deposit of iron on an electrode in revolving V.C, in a medium of composition 1.10^{-1} $mol.L^{-1}$ from acid acetic and 1.10^{-1} $mol.L^{-1}$ of sodium acetate containing $1.1O^{-1}$ $mol.L^{-1}$ ferrous chloride ($FeCl_2$): (Ø = 2 mm, number of revolutions W = 1600 r.p.m, scanning rate of the potentials = 5 $mV.s^{-1}$).

3.2 VOLTAMMETRIC STUDIES IN ORGANIC MEDIUM

The method consists in recording the voltammograms of iron cations in mode of convective diffusion to a stationary and revolving electrode. Indeed, this method must make it possible to visualize the consequences which rise from the contacts that the ions with the electrode can have. In order to cover the field of the potentials available in organic medium, the voltammograms were recorded with sweeping of the potentials being carried out initially towards the negative values then after inversion to dissolve the electrodeposed metal on the electrode (fig. 4).

3.2.1 BEHAVIOR OF FERROUS SALT

A. ON A STATIONARY ELECTRODE

The voltammetric study was carried out on a stationary electrode of vitreous carbon in contact with $FeCl_2$ $5.10^{-3}mol.L^{-1}$ in 30 ml of N,N-diméthylformamide and an electrolyte tetrabutylammonium hexa-fluorophosphate with $1.10^{-1}mol.L^{-1}$. The voltammogrammes recorded during sweeping with 100 mV/S between - 1.6 and + 1.0 V/ECS present two peaks of oxidation observed to - 0.5 and + 0.24V and two peaks of reduction observed with - 0.04 and -1.6V. The difference between the quantities of electricity Qa and Qc determined by peak integration of Fe (II) reduction and oxidation of Fe (0) in the organic medium is lower than that observed in aqueous medium. This result implies that the quantities, in organic medium, of iron deposited and dissolved are closer than compared to those obtained in aqueous medium. The difference between the quantities of electricity Qa and Qc may be due to the reduction of some impurity present in the medium.

Qa = $1.18.10^{-4}$ Coulomb
Qc = $1.54.10^{-4}$ Coulomb
Qa/Qc = 0.77

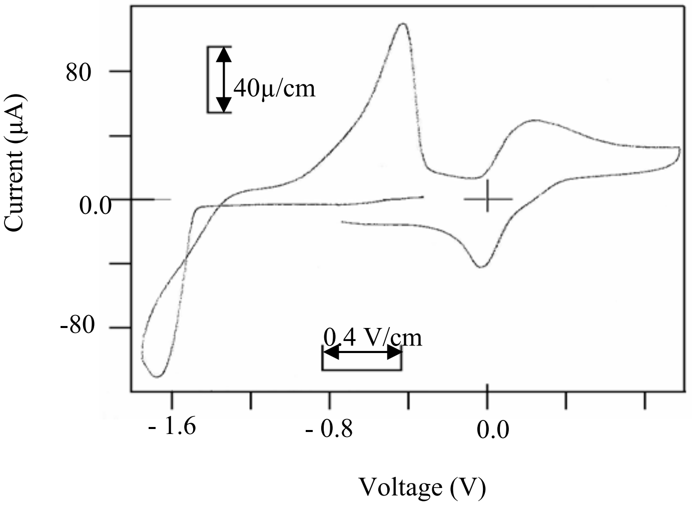

Fig.4: The cyclic voltammograms

B. ON A REVOLVING ELECTRODE

This study was carried out under the same conditions as the preceding one except that on apart from the stationary electrode which is replaced by a revolving electrode. The experiment was made with a number of revolutions of the revolving electrode equal to 1600 r.p.m and a scanning rate of 50 $mV.s^{-1}$. The voltammograms recorded (fig. 5) in the range from -1.6 to + 0.9 V present only two peaks of which one corresponds to the reduction of Fe (II) and the other to the oxidation of Fe (0). The weak difference between the quantities of electricity Qa and Qc calculated by integration of the peaks of reduction of Fe (II) and Fe (0) oxidation show that the quantities of iron deposited and dissolved are close.

$Qa = 3.75.10^{-4}$ Coulomb
$Qc = 4.65.10^{-4}$ Coulomb
$Qa/Qc = 0.80$

The replacement of the stationary electrode by the rotating electrode has improved slightly the ratio (Qa/Qc). However, the small difference between the two ratios obtained with the two types of electrodes means that the electrodeposed and dissolved quantities of iron obtained with these two electrodes are very close.

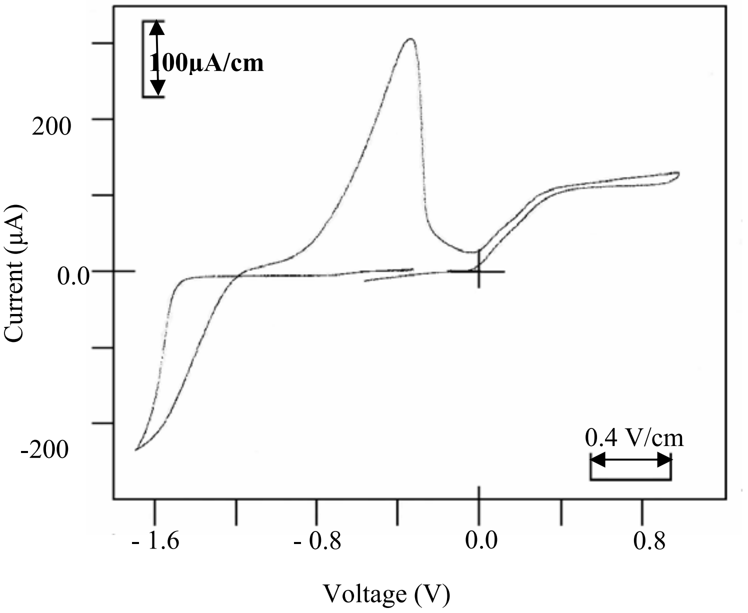

Fig. 5 **:** Voltammogram of a solution of N,N-dimethylformamide container 10^{-1} $mol.L^{-1}$ of tetrabutylammonium hexafluorophosphate, 5.10^{-1} $mol.L^{-1}$ of $FeCl_2$, Revolving electrode in V.C (Ø = 2 mm, number of revolutions W = 1600 r.p.m, Token entry, scanning rate of the Potentials: $V = 200\ mV.s^{-1}$, Thickness of the iron deposit is of 54.89 µm.

The voltammograms of oxidation de Fe (0) to Fe (II) were carried out at different scan rates of potential. The peak currents (I) obtained at different scan rates were measured. The current I (A) versus the scan rate (mV/s) is given in figure 6 wich shows that the intensity of current increases in a linear fashion with increasing the voltage scan rate.

The variation of quantity of electricity versus the reduction time of Fe (II) at Fe (0) was also studied. The method consists to stop the scanning of the potential at the reduction potential of Fe (II) to Fe (0) during a fixed time, then continue the potential scanning. The quantity of electricity was calculated for the different times of reduction tested. The quantity of electricity Q (coulomb) versus the time of registration T (s) is given in fig.7 wich shows that the calculated quantity of electricity depends on the fixed time of reduction. Indeed, the longer the applied time at the oxidation potential, the higher the quantity of electricity.

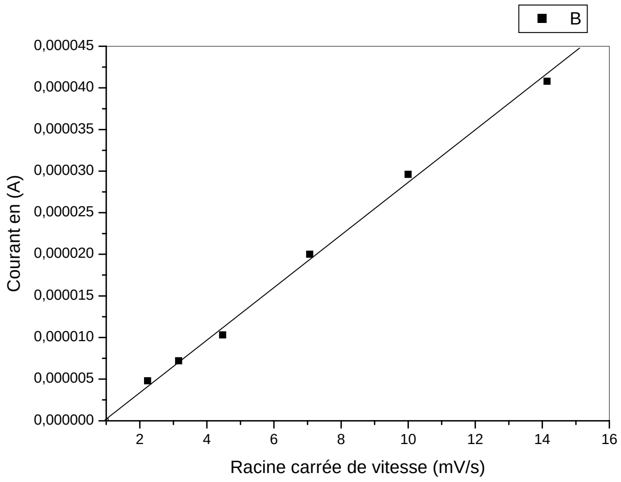

Fig.6: Influence of the voltage scan rate on current

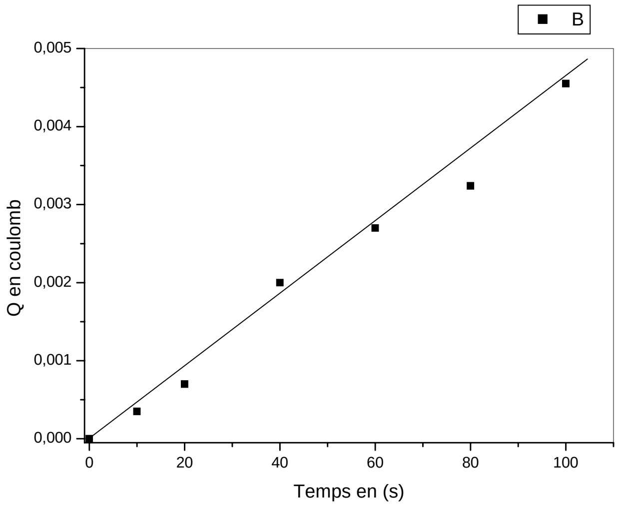

Fig.7: Q (coulomb) *vs* T (s)

Image-2: Image of the iron deposit on a revolving electrode in V. C, in a medium of D.M.F + 1.10^{-1} mol. L^{-1} of tetrabutylammonium hexafluorophosphate container 5.10^{-1} mol. L^{-1}. Ferrous chloride ($FeCl_2$), (Ø = 2 mm, number of revolutions W =1600 r.p.m Token entry, scanning rate of the potentials: V= 5 $mV.s^{-1}$)

We noticed that the layer of iron deposited on vitreous carbon electrode in organic media is much larger than that deposited in aqueous media.

CONCLUSION

This study related to the iron deposit on vitreous carbon in different media, aqueous and organic.

It was noted that in the case of the aqueous medium when the kinetics of deposit of iron is slow, the simultaneous formation of iron and hydrogen is possible with the risk of insertion of hydrogen in metal and possibly of inclusion of hydroxide $Fe(OH)_2$ in the deposit if the interfacial pH increases sufficiently.

In the case of organic medium, it was observed the kinetics of iron deposition, the problem of insertion of hydrogen does not arise. We also noticed that the layer of iron deposited on vitreous carbon electrode in organic media is much larger than that deposited in aqueous media.

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