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Fe-doped Manganese Dioxide films for supercapacitors

Tsagareli Giorgi, Makhatadze Shota, Soselia Marina and Maisuradze Nino

Page No. 125-130

The effect of the presence of Fe (II) or Fe (III) ions in solutions for obtaining thin films of manganese dioxide (MD) on their capacitive properties has been studied by the cyclic voltammetry. Optimal conditions of electrochemical method of producing films on a platinum anode have been established. Incorporation of iron ions in the crystal lattice of MD increased the capacity of the film and improved appearance of cyclic voltammogram which approached a rectangular shape. Films with the thickness up to ~150 nm after 1000 cycles lost about 10% of capacitance and retained their shape whereas for thicker films capacitive properties noticeably deteriorated.

It was shown that Fe (II) ions were chemisorbed and Fe (III) ions were adsorbed without charge transfer on the surface of the MD and thus were incorporated in its structure. At the same time, the capacity of MD films obtained in the presence of Fe (III) ions increased compared to films obtained in solutions containing Fe (II) ions. The capacity of the ~50 nm film obtained in the presence of Fe (III) ions, at 20th CV cycle was equal to 460 F/g.

Full Text

Green mediated synthesis and characterisation of dysprosium doped cadmium oxide nano particles

Shivananjaiah H.N. and Sailaja Kumari K. P.

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Dysprosium-doped CdO nanoparticles [Cd1−xDyxO] were studied to enhance and control their multifunctional properties for various optoelectronic or magneto electrical properties. After synthesizing well-defined Dy-doped CdO nanoparticles by combustion route using Euphorbia Milli latex as reducing agent, the optical and magnetic characteristics of synthesized nanoparticles were analysed. Formation of cubic structured Dy-doped CdO nanoparticles was recognized by PXRD studies and morphology by transmission electron microscopy (TEM).

The effect of increase in dopant concentration on the band gap was confirmed by UV-Vis spectra. FTIR studies confirmed the purity of the sample. In magnetic studies, room-temperature ferromagnetism (RTFM) behaviour was observed.

Full Text

Biodegradation of Dioxin and Furan from Sludge Wastewater Treatment of Pulp Industry by Phanerochaete chrysosporium

Henggar Hardiani and Teddy Kardiansyah

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The chlorinated organic compounds in the wastewater are formed from the bleaching process in pulping. These compounds are dioxins and furans known to be toxic and carcinogenic and persistent environmental pollutants with bio-accumulative properties and provide a risk of adverse effects on human health and the environment. Beside that they have the potential to migrate through soil, water and air. Disposal of sludge from WWTP by open dumping has the potential to cause environmental problems such as soil pollution, groundwater and surface water. Because of the toxicity of dioxins, how to remove dioxins from polluted environments is one of the most challenging problems in environmental technology. This research aims to determine the potential of Phanerochaete chrysosporium fungi to be able to degrade dioxins and furans. The characteristics of waste sludge from WWTP contains high EOX compounds of 957.0 µg/g, organic content of 83.89%; 2.3.7.8-Tetrachlorodibenzodioxin is <0.0011 µg/g; Octachlorodibenzodioxin 0.2 µg/g; and Octachlorodibenzofuran around of 0.25 µg/g.

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Fe-doped Manganese Dioxide films for supercapacitors

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Abstract
The effect of the presence of Fe (II) or Fe (III) ions in solutions for obtaining thin films of manganese dioxide (MD) on their capacitive properties has been studied by the cyclic voltammetry. Optimal conditions of electrochemical method of producing films on a platinum anode have been established. Incorporation of iron ions in the crystal lattice of MD increased the capacity of the film and improved appearance of cyclic voltammogram which approached a rectangular shape. Films with the thickness up to ~150 nm after 1000 cycles lost about 10% of capacitance and retained their shape whereas for thicker films capacitive properties noticeably deteriorated.

It was shown that Fe (II) ions were chemisorbed and Fe (III) ions were adsorbed without charge transfer on the surface of the MD and thus were incorporated in its structure. At the same time, the capacity of MD films obtained in the presence of Fe (III) ions increased compared to films obtained in solutions containing Fe (II) ions. The capacity of the ~50 nm film obtained in the presence of Fe (III) ions, at 20th CV cycle was equal to 460 F/g.

Keywords: Supercapacitor, Manganese Dioxide Film, Doping, Electrodeposition, Cyclic Voltammogram.

Introduction

Nowadays, electrochemical capacitors are becoming promising energy storage systems, especially for high power devices. This class of current sources is called supercapacitors or ultracapacitors. They occupy an intermediate position between traditional capacitors and batteries. Supercapacitors (SC) are energy storage devices with a higher energy density than conventional capacitors and with a higher power density than batteries[5,8,10,15]. SCs are used in many branches of industries such as hybrid cars, cell phones, navigation devices etc. Their main purpose is increasing the battery life. SCs are characterized by good reversibility and cycling duration. Generally, two energy storage mechanisms are considered: the double layer capacitance and the Faraday pseudo capacity.

In the first case, the separation of opposite charges occurs at the interface between the electrode and electrolyte. In the second, pseudo-capacitance is caused by a fast reversible electrochemical reaction at the surface of the electrode with a change in the oxidation number of the active material. For the first type of SC, materials such as various types of carbon with a highly developed surface and conductive polymers are used[7,17]. In the case of using a pseudo-capacitive mechanism, as a rule, transition metal oxides are used[7-9]. The best of them, ruthenium dioxide is characterized by the highest capacity[12,13,21,22]. However, due to the high cost and aggressivity of the electrolyte used, its commercial use is limited.

Lee and Gudenov[11] showed that the powder of amorphous manganese dioxide (MD) introduced into the structure of the composite electrode exhibits electrochemical properties similar to the behavior of conventional electrostatic capacitors. After this publication, interest in MD as an active material for the SC increased significantly[2].

MD is a non-stoichiometric compound with many modifications that differ in crystal structure or amorphousness, grain size, presence of impurity ions, presence of structural or adsorption water, crystal vacancies and so on. Structural differences determine the properties of MD including electrodic characteristics. Electrodeposition of MD from solution, containing Mn (II) ions, is complicated reaction with various chemical and electrochemical stages[9,14]. The mechanism of reaction and properties of obtained product are depended on reaction conditions such as the composition of the solution, temperature, current density etc.

Thus, by purposefully changing the methods and conditions during the synthesis of MD, it is possible to obtain a material with the desired electrochemical properties. For SC, pseudocapacity of thin film is used. The film should be mechanically and chemically resistant, not destroyable in a fairly wide range of potentials and multiple cycling.

Material and Methods

Anodic deposition of thin MD films and the study of their electrochemical properties were carried out in a standard three-electrode cell. The platinum wire with a diameter of 1 mm and a length of 10 mm was used as a working electrode. The counter electrode consisted of a platinum plate. Ag/AgCl electrode was used as a reference electrode. The formation of the film was carried out in a solution of 0.002 M $MnSO_4$ + 0.195 M Na_2SO_4 + 0.005 M H_2SO_4 with the addition of the appropriate concentration of iron (II) or (III) sulfate. The films were deposited at a potential of 1.2 V versus Ag/AgCl electrode in the coulometric mode.

Since the electrochemical method of producing MD was developed almost immediately, it became known that the admixture of iron ions in the electrolyte solution causes a significant decrease in the MD's current efficiency. At the same time, the current efficiency of the product decreases with increasing of iron concentration[19]. Therefore, it was

impossible to calculate the mass of the film by the amount of electricity spent on its formation.

To estimate the mass and consequently the film thickness, MD was electrochemically completely dissolved in coulometric mode and its approximate mass was found by the amount of consumed electricity. When calculating the film thickness, the density of the MD was taken to be 4.2 g / cm^3. This value may differ depending on the modification of the MD especially for a thin film. Therefore, the obtained values are approximate.

The properties of the obtained films were studied by cyclic voltammetry in a 0.5 M Na_2SO_4 solution, the scan rate was 50 mV/s. Before measurements, the electrode was periodically subjected to anodic-cathodic polarization in the potential range from oxygen evolution to hydrogen evolution in a 0.5 M H_2SO_4 solution. The capacity of the film was calculated using the following equation:

$$C = \frac{I\Delta t}{\Delta V m} \quad (1)$$

where I is the current, Δt is the potential sweep time, ΔV is the voltage interval and m is the mass of the film. $I\Delta t$ was determined from half of the area obtained by cyclic voltammogram.

For the preparation of working solutions, twice distilled water was used. The used salts were further purified by recrystallization and sulfuric acid by distillation. The measurements were performed on a PalmSens 4 potentiostat and the GWP-673 universal polarograph.

Results and Discussion

The choice of iron as a modifying agent was predetermined by the previously obtained results. It was shown that during electrodeposition of MD in the presence of Fe (II) in the electrolyte solution, iron was introduced into the MD structure. The iron content in MD film increased in proportion to its content in solution. The resulting modification significantly changed the electrode properties. As the iron content in MD increased, the polarization of the electrode increased and oxygen evolution began. This was the main reason for the decrease in the current efficiency of the MD and not the alternating oxidation and reduction of iron ions at the anode and cathode respectively as was previously thought.

When the iron content in MD reached 5%, its electrodeposition practically ceased. However, when replacing the electrolyte with a solution that did not contain iron, the current efficiency of the MD on such an electrode gradually increased and reached the usual value close to 100%. At the same time, the activity of MD in the battery did not practically change[19].

In fig. 1, cyclic voltammograms of MD films unmodified and modified with iron are shown. The obtained experimental results showed that the introduction of iron ions into the MD crystal lattice increased the capacity of the film and improved the shape of the cyclic voltammogram which was close to the ideal rectangular shape for the SC. This difference became especially noticeable with increasing of film thickness.

During the electrodeposition of MD in the presence of iron ions, their alternative oxidation and reduction at the anode and cathode respectively occurs. Therefore, both types of iron ions are always present in the solution. To study the effect of only Fe (III) ions in the electrolyte solution on the property of the resulted MD film, a cell with a separated anode and cathode spaces was used. In present work, the influence of the concentration of Fe (III) ions and the electrodeposition potential of the MD film were investigated. An optimal result was obtained for the MD film which was formed in the presence of 0.001 M Fe (III) at a potential of 1.2 V.

The presence of only Fe (III) ions in the solution increased the capacity of the film which can be explained by more sufficient decreasing of the efficiency of MD film during its formation in the presence of Fe (II) (Fig.2). The capacity of a ~50 nm film obtained in the presence of Fe (III) ions at the second cycle was more than 500 F/g and by 20th cycle was 460 F/g after which remained stable and practically unchanged.

In studying the mechanism of iron doping into the MD structure, the MD film was deposited from solutions that did not contain iron ions. The resulting electrode was subjected to anodic polarization in a solution of 0.5 M Na_2SO_4 at a potential 1.4 V in order to oxidize manganese ions of a lower oxidation number to MD on the surface of the electrode. Then, the Pt/MnO_2 electrode was kept in a solution containing only Mn (II), Fe (II) or Fe (III) ions, thoroughly washed with water and the anodic polarization curve was recorded as in fig. 3. In the case of holding the electrode in solutions of Mn (II) and Fe (II), peaks of anodic currents were observed in the region of the electrodeposition potential of MD. After keeping the electrode in the Mn (II) solution, we explained by the chemisorption of Mn (II) ions on the surface of the MD with the subsequent oxidation of the chemisorbed particle to MD.

$$MnO_2 + [Mn(H_2O)_6]^{2+} \rightarrow MnOOH\cdot[Mn(H_2O)_5OH]^{2+}_{ads} \quad (2)$$

$$MnOOH\cdot[Mn(H_2O)_5OH]^{2+}_{ads} \rightarrow 2MnO_2 + 4H^+ + 4H_2O + 2e \quad (3)$$

The hydrolysis of hexaaquaions of Mn (III) was investigated and it was shown that dissociation constant of the first stage of hydrolysis was K = 0.88. Thus, even in quite strong acidic solutions, $[Mn(H_2O)_5OH]^{2+}$ ions are formed in significant amount. Clark et al[3] mentioned ease of hydrolysis of $[Mn(H_2O)_6]^{3+}$ ions, pKa = 0.03 and based on these results justify existence of absorbed $[Mn(H_2O)_5OH]^{2+}$ particles on

the MD surface. However, in difference to our assumption, these authors admit that Mn (III) ions are formed as a result of electrochemical oxidation of Mn (II).

We assume that in the case of keeping the Pt/MnO_2 electrode in a solution of Fe (II) ions, they are chemisorbed along the same lines with the formation of $MnOOH{\cdot}[Fe(H_2O)_5OH]^{2+}_{ads}$. The anodic peak in this case should be less because oxidized Mn (III) particles on the surface of MD are half as much as during the chemisorption of Mn (II). When the Pt/MnO_2 electrode is kept in a solution of Fe (III), apparently their simple adsorption without charge transfer occurs; therefore, in this case no anodic peaks were observed, the current was even lower than the background value (Fig. 3).

The influence of the concentration of Fe (III) ions in the electrolyte solution for obtaining the MD film on its capacity is shown in fig. 4. It can be observed that the optimal concentration is 0.001 M Fe (III). The redox reaction occurring during cycling of the DM film can be represented by the equation:

$$MnO_2 + xe^- + xH^+ = H_xMn_x^{III}\,Mn_{1-x}^{IV}O_2 \qquad (4)$$

The electrical conductivity of the MD is not very high and with increasing of film thickness, the electrical resistance increases as well. In addition, diffusion limitations of the proton in the solid phase of the MD. Many authors consider the diffusion of a proton occur in the solid phase of the MD as a slow stage which limits the speed of the process[1,4,6,16].

Fig. 5 shows the dependence of the capacity of the MD film on its thickness. As can be seen from this figure, the capacity of the film of unmodified DM weakly depended on its thickness while the capacity of the modified film is increased with its thickness. From the obtained results, it follows that in the studied conditions, the redox process in the case of iron undoped MD occurs near the electrode surface while in the iron-modified MD film, "works" the film's volume. Apparently, the introduction of iron into the MD structure increases the electrical conductivity of the film, but most importantly facilitates solid-phase diffusion of the proton. MD characterized by semiconductor properties. Therefore, such significant influence of iron impurities on the electrode properties of MD is quite explicable.

For films with the thickness of ~50, 100 and 150 nm, 1000 cyclic voltammograms were taken. For each film, the total cycling time was more than 9 hours. The dependence of the film capacity on the number of cycles is shown in fig. 6. For films with the thickness of ~50 and 100 nm, the loss of capacity during cycling was about 10%. At the same time, the capacity of the films after ~20 cycles remained almost unchanged. The shape of the cyclic voltamogram also remained almost the same close to the rectangle. These data are evidence of the good reversibility of the oxidation-reducing reaction as well as of the chemical and mechanical strength of the film.

The third film under similar conditions quickly lost its capacity, especially in the initial period of cycling and by the end of cycling, only 35% of the initial value was left. At the same time, the shape of the curve was significantly distorted. Thus, it can be concluded that films with the thickness of more than 150 nm can hardly be used as an electrode material for SC.

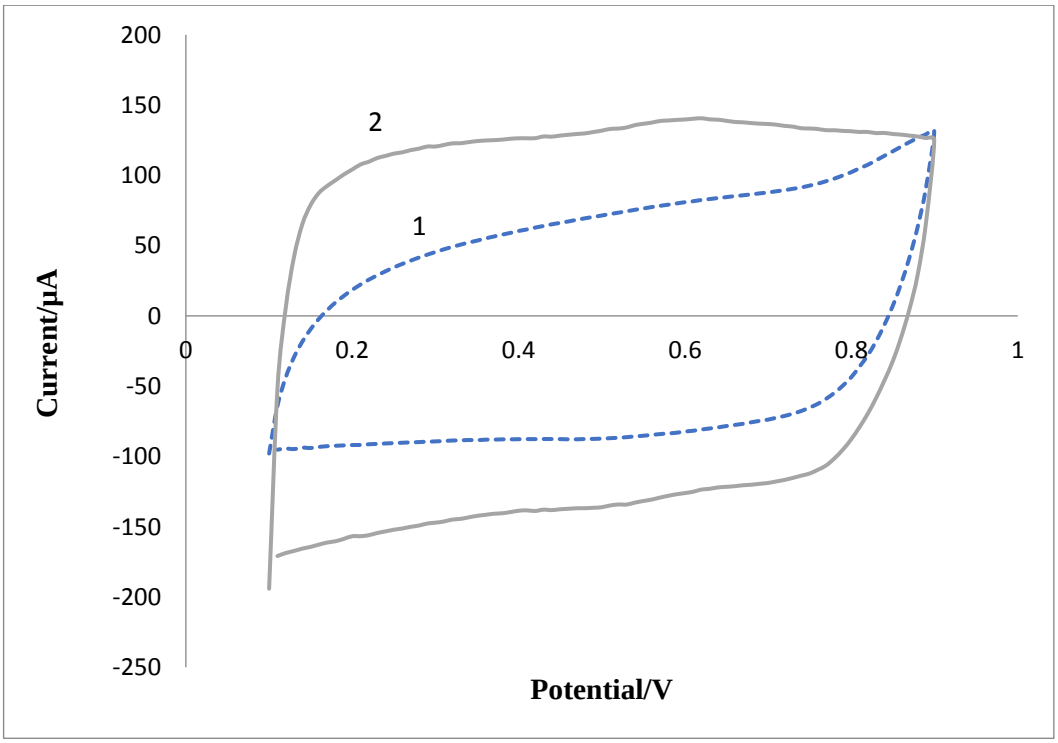

Fig. 1: Cyclic voltamogramm of MD film: 1 – unmodified MD; 2 – modified MD with iron.

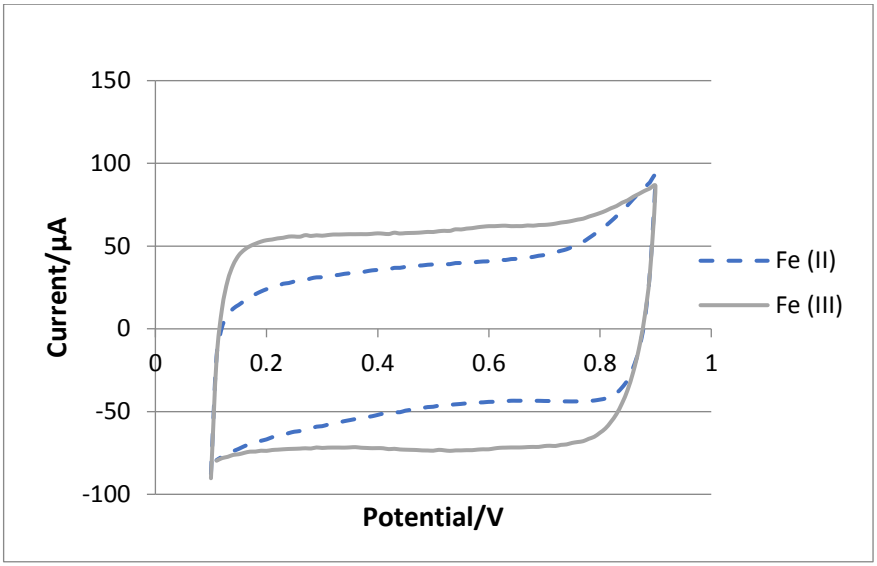

Fig. 2: Cyclic voltamogramm of MD film doped with Fe (II) and Fe (III).

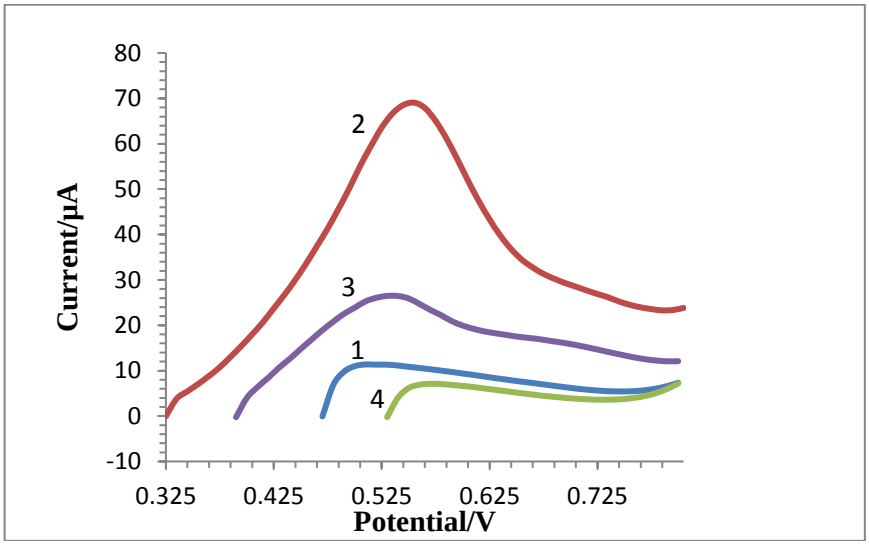

Fig. 3: Voltametric curves of Pt/MnO_2 electrode in 0.5 M Na_2SO_4. 1- Pt/MnO_2 preliminary polarized in 0.5 M Na_2SO_4 solution at 1.4 V. Electrode was kept in: 2 - 0.005 M Mn (II); 3 - 0.005 M Fe (II); 4 - 0.005 M Fe (III).

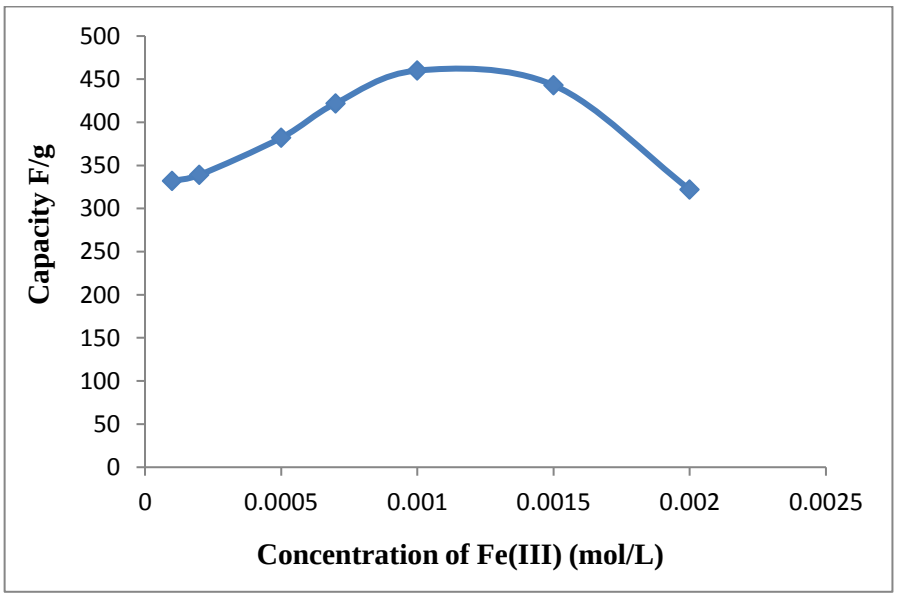

Fig. 4: Dependence of capacity of the MD film on concentration of Fe (III) ions.

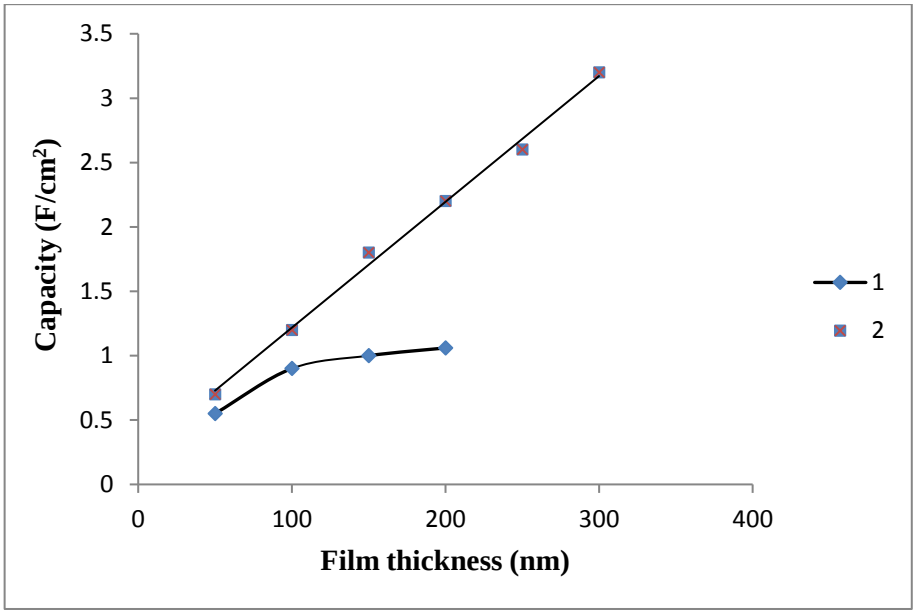

Fig. 5: Dependence of capacity of the MD film on film thickness. 1-unmodified MD; 2-modified with Fe (III) ions.

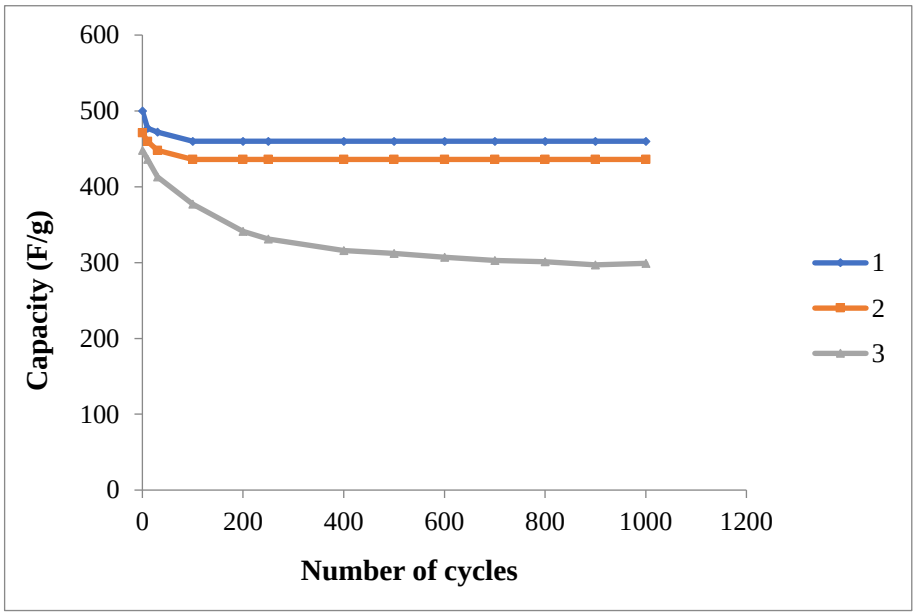

Fig. 6: Dependence of capacity of the MD film with different thickness on the charge-discharge cycles: 1-film thickness ~50 nm; 2 – ~100 nm; 3- ~150 nm.

Conclusion

1. The introduction of iron ions into an electrolyte solution for obtaining of MD leads to an increase in the capacity, duration of cycling and durability of the MD film.
2. Fe (II) ions are chemisorbed and Fe (III) ions are adsorbed without charge transfer on the surface of the MD and thus are incorporated into its structure.
3. The replacement of Fe (II) ions with Fe (III) in the electrolyte solution significantly improved the capacitive properties of the MD films and the shape of the cyclic voltammogram was ameliorated.
4. The loss in capacitance of thin MD films after 100 cycles was 10% while the MD film more than ~150 nm thick quickly lost a significant part of the capacitance wherein the shape of the cyclic voltammogram was deteriorated.

Acknowledgement

The work was carried out with the financial support of the Shota Rustaveli National Science Foundation of Georgia within the framework of the Fundamental grant No. FR17_478.

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(Received 24th October 2019, accepted 22nd December 2019)

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