

Clay Modified Conductive Electrodes

Nilar Kyi*, S.Sladkevich[†], Ovadia Lev^{††}

**Department of Chemistry, Dagon University, Myanmar*

[†]The Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem, 91904, Israel

^{††}The Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem, 91904, Israel
nilar.kyi@gmail.com, sladkevichs@gmail.com, ovadia@mail.huji.ac.il

Abstract. The conductive and transparent porous composite electrode was introduced. The electrode materials were composed of antimony doped tin oxide (ATO)-coated clay platelets imbedded in sol gel derived silicate. The platelet clay self-aligned in a layered structure within the silicate film, an anisotropic construction that minimizes the ATO loading required to achieve electric percolation. In order to demonstrate the differences in the electrochemical behavior two types of mica composite electrodes were prepared. The electrochemical capabilities of such electrodes; Clay Modified Electrodes (CMEs) were studied by using Cyclic voltammetry technique. Addition of Single Walled Carbon Nanotubes (SWCNT) to Mica-based films as a way to improve conductivity was also studied.

Keywords: Clay Modified Electrodes (CMEs), Cyclic voltammetry technique, Single Walled Carbon Nanotubes (SWCNT)
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INTRODUCTION

Metal ceramic and metal hydrogel composites as well as thin metal impregnated layers are increasingly used, partly owing to the evolution of nanomaterial electrochemistry, which brought about a plethora of new ways to prepare nanoparticles, functionalize them, and produce intricate constructions of metallic nanoparticles by sol-gel or other binding gels or by bridging molecules.

In this work, a new form of conductive and transparent porous composite electrode is introduced by using the anisotropy of mica flakes it is possible to produce transparent and conductive permeable, sol-gel-derived silicate-mica clay electrodes at (or close to) room temperature. The starting material for electrode construction is a dispersion of antimony-doped, tin oxide-coated mica flakes (commercially available) in sol-gel-derived silicate or methyl silicate binder. Clay-modified electrodes are by no means new to electrochemistry. The first works on the subject date back to the seminal papers of Bard's team in the mid 1980s [1]. Clay composites have practical importance for catalysis in the oil industry [2, 3], where mesoporosity, gained by delamination and partial loss of the long range order, is desirable. Mesoporosity is vital for enhanced mass transport. Another major field of application is polymer science where strength and toughness was the driving force for the introduction of clay-polymer composites [4]. Soon enough, research accounts of the enhancement of optical properties (refractive index, nonlinear optics, luminescence) and thermal properties followed the nylon-6 composite studies [5, 6]. Of relevance to the current project is also the use of organo-clays as potent absorbers for environmental pollutants [7]. Different sections of this background will describe the intersection between sol-

gel technology and clay minerals and the formation of **Clay Modified Electrodes (CMEs)** by sol-gel and other technologies. It should be noted however, that the major fields of application of clays minerals today require conditions that are vastly different from those required in this project, namely electric conductivity and high transparency.

This work combines several research fields aiming eventually at the introduction of a general new class of anisotropic-conductive materials via intercalated, pillared or otherwise chemically modified clay minerals. Common to all of the proposed applications is the need for transparency and conductivity and for the most part also porosity. This research described the state of the art of clay modified electrodes and relevant fields of sol-gel science as well as the particulars of the electrochemical demonstrative applications.

Aims and Objectives of Present Works

Aim of the present work is using aluminosilicate clays to improve conductivity of electrodes and to be used in electrochemical applications The objectives of the present work are;

- To optimize the procedures for ATO (antimony doped tin oxide) coating on mica
- To make thin films with ATO-coated mica in PVDF and sol-gel silicate binders and their characterization
- To build CMEs (clay-modified electrodes) with ATO-coated clays and their characterization with simple electroactive species
- To prepare composite films of ATO-coated clays with Carbon Nanotubes (CNTs)
- To use CMEs in electrochemical applications

MATERIALS AND METHODS

All chemicals used in this research were purchased from BDH Chemicals Ltd. (Poole, England). Microscope glass slides were purchased from Medipan, (Berlin, Germany). ITO-coated, 7×50×0.7 mm unpolished float glass used from Delta Technologies Ltd. (Stillwater, MN). ATO-modified mica platelets, Minatec 31, were purchased from Merck. Electrochemical studies were conducted using cyclic voltammetry technique. Serion HR SEM equipped with a Schottky FEG gun electron probe was used for scanning electron microscopy (SEM) and for elemental analysis. A Cary1 UV/vis spectrophotometer from Varian (Mulgrave, Australia) was used for transparency studies.

RESULT AND DISCUSSION

A Route for ATO Coating on Mica Platelets – Development and Optimization

There are a several procedures for preparation of conductive antimony doped tin oxide (ATO) films on glass substrates. This work used a modified Pechini's method for the preparation of mica platelets, coated by ATO. Precursor preparation technique was adopted from Bernardi et.al.[8]. Tin (II) chloride and antimony (III) chloride dissolved in ethanol to produce 10 mole% ratio Sn:Sb. The solution was stirred and heated (60-70°C) for 2 hours. Then citric acid and ethylene glycol were added in a molar ratio of 8:1:2 (ethanol : citric acid : ethylene glycol) and the mixture heated and stirred additional 3 hours, This precursor is filtered and added by dropwise to mica suspension in water under stirring and heating (60-70°C). After 22 hours the coated mica suspension is washed with ethanol, dried by vacuum pump and calcinated in the oven (400-800°C) for 3 hours. The obtained grey powder was used to make a conductive semi-transparent films on glass by incorporation in either sol-gel silicate or PVDF (polyvinylidene difluoride) matrix.

SEM images of mica-M (the trade name of uncoated mica), commercially available ATO-coated mica platelets – Minatec 31 (Merck), and ATO-coated mica, produced by the modified Pechini method, are presented in Figures. 1A-C. Figures 1.E and 1.F depict the EDX spectra of the commercial and lab coated mica surface. Although the micrographs of the commercial and home prepared samples are very similar the tin loading is larger in the commercial sample (as can be seen from Sn/Si ratio) and the doping level Sb/Sn is also higher for the commercial sample. Figure 1.D is a SEM image of the cross-section of ATO-coated mica (produced by the modified Pechini route) in PVDF polymer. It can be

seen that the surface is flat (left part of the figure) and the layered structure can also be discerned in the cross section part (in the middle of the frame).

In order to check the calcinations temperature influence on optical and electrical properties of the pigment to carry out a series of identical experiments when in the final step of heat treatment the temperature changed in the range 400-800°C. The conductivity and optical density of thin films prepared by PVDF technique were measured and the optimal temperature range for heat treatment have been chosen (Figures 2 and 3).

The properties of the mica-ATO thin films in PVDF and sol-gel matrix were compared to those of commercially available conductive mica pigment (Minatec 31 of Merck, figure 4). As can be seen from the figure both sol-gel and PVDF binder films with mica-ATO (prepared by modified Pechini's route) have better conductivity and lower transparency compared to Minatec 31 films.

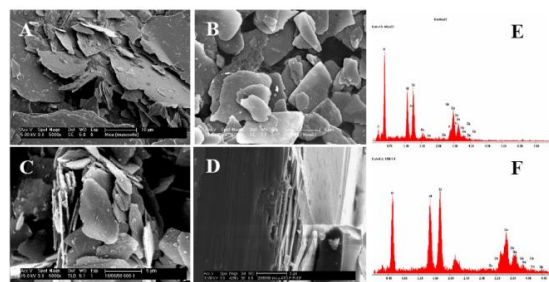


FIGURE 1.(A) Mica-M (Merck) clay powder. (B) Minatec 31(Merck). (C) ATO coated Mica-M by modified Pechini route. (D) ATO coated Mica-M (modified Pechini route) incorporated into PVDF polymer matrix. (E) EDX spectrum of Minatec 31 platelet surface. (F) EDX spectrum of ATO-coated (modified Pechini) mica platelet surface.

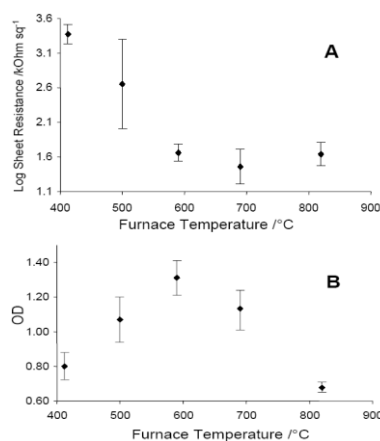


FIGURE 2. The dependence of sheet resistance (A) and optical density (B) of mica-ATO films in PVDF matrix on calcination temperature (wavelength 500 nm).

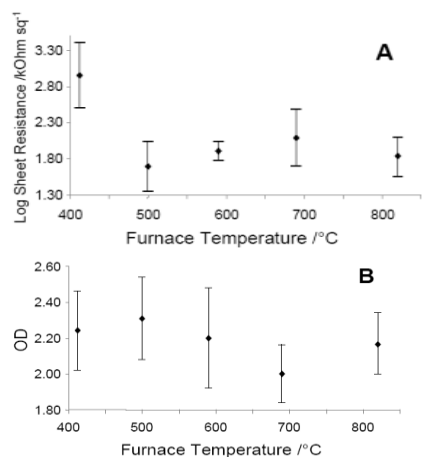


FIGURE 3. The dependence of sheet resistance (A) and optical density (B) of mica-ATO films in sol-gel matrix on calcination temperature (wavelength 500 nm).

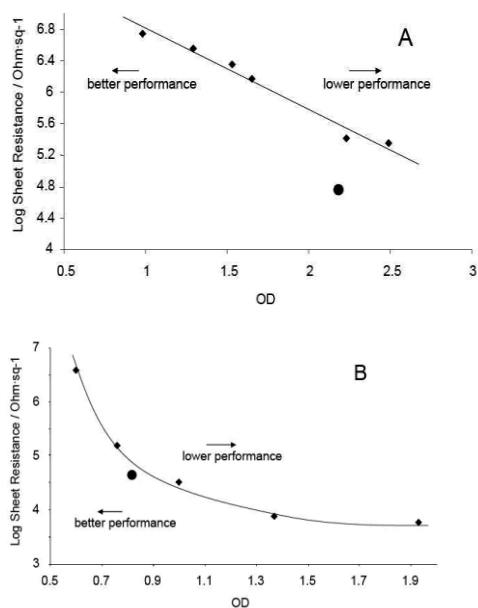


FIGURE 4. Logarithm of sheet resistance vs optical density for Minatec31 films in sol-gel silicate (A) and PVDF (B) matrix. Circles—mica-ATO (Pechini)films in sol-gel silicate (A) or PVDF (B) matrix (wavelength 500 nm).

This research investigated another precursor preparation procedure for ATO-coated mica, which was based on the route, described by Guzman et.al. [9] for glass substrate coating. Ethanol solution, containing tin (II) chloride, antimony (III) chloride, and diacetone alcohol (DAA), was heated and refluxed 2 hours. Then it was added dropwise to water mica suspension during 4 hours under heating (60-70°C) and stirring. The suspension stirred overnight, washed, and dried by vacuum pump. Dried powder was calcinated 2 hours in the oven at 600°C. The obtained

grey powder was used to make conductive semi-transparent films on glass by incorporation in PVDF matrix. Properties of films prepared with all types of ATO-coated clays (Minatec31, ATO-mica by modified Pechini method, ATO-mica by DAA method) are listed in Table 1.

TABLE 1. Properties of sol-gel silicate and PVDF conductive films, prepared with different types of ATO-coated mica.

ATO-coated clay	Sn/Sb molar ratio (by EDX)	Sol-gel silicate binder (n=9, p=0.95)		PVDF binder (n=9, p=0.95)	
		Log Sheet Resistance, kOhm/sq	OD (at500nm)	Log Sheet Resistance, kOhm/sq	OD (at500nm)
Minatec 31	2.89±0.37 (n=3)	2.22±0.22	2.28±0.11	2.24±0.20 (n=6)	0.75±0.08 (n=6)
Pechini	9.70±5.28 (n=3)	1.82±0.18	2.17±0.13	1.64±0.13	0.80±0.17
DAA	16.06±5.64 (n=6)	1.84±0.24	2.74±0.24	1.64±0.19	1.24±0.14 (n=3)

OD- Optical Density Error margins represent 95% confidence interval.

Electrochemistry of Porous, Conductive and Semitransparent Clay-based Electrodes

In order to demonstrate the differences in the electrochemical behavior, two types of mica composite electrodes were prepared. Specified amount of Minatec 31 was added to the freshly prepared silicate (TMOS, tetramethyl orthosilicate) or methyl silicate (MTMOS, methyl trimethoxysilane) precursors. Then ITO (Indium doped tin oxide) glass slides were coated with the dispersion by dip coating technique and dried in the oven. The permselectivity of these composite films was demonstrated using the positively charged methyl viologen (MV^{2+}) and a negatively charged hexacyanoferrate couple. The reduction of MV^{2+} on the TMOS-derived electrode (Figure 5.A) obeyed quasi reversible behavior over a large range of scan rates. The inset of frame A shows a linear dependence (correlation coefficient $R^2 = 0.973$, $n = 12$) of the faradic current on the square root of the scan rate. The reduction of MV^{2+} on methyl silicate electrodes shows very different behavior, as can be readily observed in Figure 5.B. Instead of the quasi reversible behavior of the silicate electrode, methyl silicate-based electrode shows current waves (with no current peaks) around the formal potential of MV^{2+}/MV^+ . The cyclic voltammetry curves of the negatively charged hexacyanoferrate probes are depicted in Figure 6.A

and B. The oxidation and reduction peaks for both hydrophilic and hydrophobic electrodes are very small. For the ATO/clay silicate composites, the peaks are almost symmetrical, showing that the hexacyanoferrate couple is collected from very small domains in the vicinity of the active sites or even absorbed on the active site. Clearly, the negatively charged hexacyanoferrates are rejected by the negative charges on the ATO/mica/silicate surfaces, which is manifested in much smaller faradic currents compared to those exhibited for the positively charge probe in Figure 5.A. The double layer capacitance is, of course, unaffected by the probe molecule used, and the methyl silicate background current remains much smaller for the hydrophobic electrode compared to the hydrophilic silicate electrodes. Figures 5 and 6 clearly demonstrate that the composite ATO/mica silicates, and to some extent also ATO/mica methyl silicate electrodes, exhibit a large preference for positively charged probes. Similar behavior was reported by Hsueh et.al.[10].

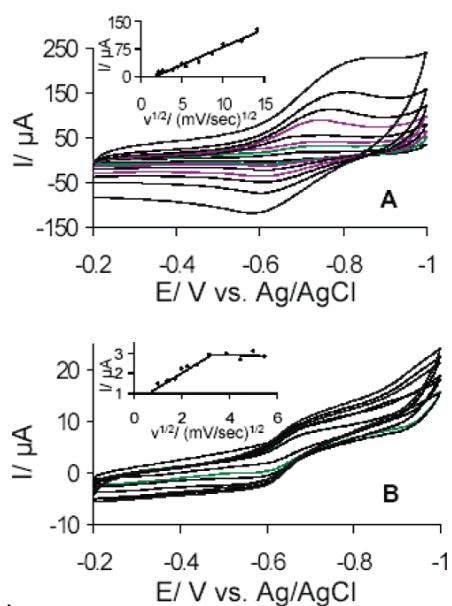


FIGURE 5. Cyclic voltammetry of 1 mM methyl viologen in 0.01 M KNO_3 , pH 6.5, at different scan rates. (A) Silicate-based electrode (1, 2, 3, 5, 7, 10, 20, 30, 50, and 100 mV/s in intuitive order) and (B) methyl silicate-based ATO/mica electrode (curves correspond to 1, 3, 5, 7, 10, 15, 20, 30, and 40 mV/s). Insets depict the scan rate dependence of the faradic current. The measurements were carried out in a three electrode cell using saturated Ag/AgCl reference, graphite counter, and the transparent composite electrode as working electrode.

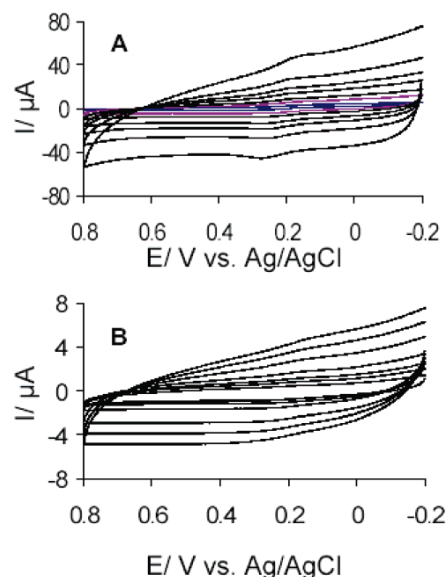


FIGURE 6. Cyclic voltammetry of 1 mM hexacyanoferrate in 0.1 M KNO_3 , pH 6.5 as a function of scan rate on (A) silicate-based ATO/mica electrode (curves correspond to scan rates 1, 5, 10, 20, 30, 50, and 100 mV/s in intuitive order) and (B) methyl silicate-based electrode (scan rates: 5, 10, 15, 25, 50, 75, and 100 mV/s). The measurements were carried out in a three electrode cell using saturated Ag/AgCl reference, graphite counter, and the transparent composite electrode as working electrode.

Addition of CNT to Mica-based Films as a Way to Improve Conductivity

Carbon nanotubes (CNTs) are of great interest nowadays due to their physical properties and possible applications in chemical sensors and nanoscale devices. Their high conductivity makes CNTs excellent fillers in conductive composites. As can be seen from figure.7, addition of small amounts of CNT to clay composites reduces sheet resistance by one order of magnitude. The optical density at the same time increases slightly.

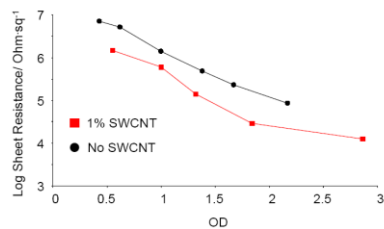


FIGURE 7. Logarithm of sheet resistance vs optical density for Minatec31 films in sol-gel methyl-silicate with (red line) and without addition of single-walled CNT (black line) (thickness of film 20 μm , wavelength 550 nm).

CONCLUSION

Intercalated clays and particularly organic-inorganic composites that are formed by the penetration (intercalation) of cations and polymers have attracted much attention. They are already used in many scientific fields and in the industry. The excellent advantages of clay platelets could be used to produce conductive and semitransparent porous electrodes at moderate temperatures. The most useful approach is to use doped tin oxide based conductive films. It was found that due to the anisotropy of the antimony doped tin oxide (ATO) coated mica clay can bring about electrode conductivity using almost two orders of magnitude lower loading of ATO compared to the experimental percolation threshold of ATO in clay-free homogenous sol-gel silicate matrix.

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