

Study of the Anodic Dissolution Solutions of Single Crystals of Molybdenum Diselenide (MoSe₂) in KOH Media

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ABSTRACT

This work is a contribution to the study of semiconductor materials that are used in semiconductor electrolyte junctions for the conversion of light energy into electrical energy. The study was carried out in KOH medium on single crystals of molybdenum diselenide obtained by physical vapor transport and previously characterized by different analysis techniques (SEM, XRD, etc.). A preliminary study on standard molybdate ion solutions was first carried out in order to establish the potential domain of molybdate ions. Cyclic anodic redissolution voltammetry was used for the analysis of standard solutions and MoSe₂ dissolving solutions obtained by anodic attack at fixed potential. The results obtained show a reduction peak towards -0.812V indicating the deposit during the pre-electrolysis. A first oxidation peak at around -0.740V and a secondary peak at around -0.429V corresponding to the oxidation of the deposit during redissolution. Analysis of the results shows that MoSe₂ is not stable in KOH media.

Keywords: Cyclic voltammetry; Molybdenum diselenide; anodic attack; KOH medium.

INTRODUCTION

The two-dimensional (2D) structural lamellar dichalcogenides of transition metals MX₂ (M = Mo, W... and X = S, Se, Te) are the subject of much research in the fields of photovoltaics, photocatalysis, electronics, and thermoelectric, due to their many unprecedented chemical and optoelectronic properties that are inaccessible in many materials [1-8]. They are generally synthesized either by crystal growth by physical vapor transport [9-13] or by electrodeposition in ionic media [14-19]. In the present work, the material studied is a single crystal of molybdenum diselenide (MoSe₂) obtained by chemical vapor transport with tellurium tetrachloride (TeCl₄) [9]. It has previously been characterized by different physical methods (Scanning electron microscopy (SEM), X-ray diffraction (XRD), etc.) and these semiconductor properties have been studied by measuring electrical conductivity and photo-current [9]. The results obtained augur well for the use of the material as a working electrode in an electrochemical photo cell for applied purposes. However, for a better use of the properties of the semiconductor/electrolyte junction for use such as the conversion of solar energy into electrical energy, the study of the semiconductor/electrolyte junction must put the emphasis on the anodic dissolution of the material at fixed potential.

Indeed, the phenomenon of the dissolution of materials during electrolysis is a major problem with all semiconductor electrodes and represents the main obstacle to their use in electrochemical cells for applied purposes. It is therefore interesting to carry out any study of the behavior of the material in various electrolytes under anodic polarization. The present work is part of this dynamic. It consists in studying the behavior of MoSe₂ in an electrolytic medium by studying its dissolution by anodic attack at a fixed potential of 1.2 V for 24 hours in a basic media. This will allow precise determination of the balance sheet of the charge transfer reaction at the semiconductor/electrolyte interface in order to implement surface treatment means in order to improve the performance of the MoSe₂/junction. electrolyte.

MATERIAL AND METHODS

Equipment

The potentiostat used in this work is Radiometer analytical, voltalab PST050. It is directly controlled by a computer equipped with a voltamaster 4 program. Its role is to ensure automatic regulation of the potential difference imposed between the reference electrode and the electrode under study. The measuring cell is associated with an MDE 150 type polarographic stand which allows automatic control of the measurements. The cell is essentially made up of three electrodes:

- a working electrode with a rotating disc with a glassy carbon tip, 3 mm in diameter;
- a reference electrode for silver chloride Ag/AgCl (3M KCl) type TR020 from Radiometer analytical brand. Its potential is 208 mV relative to the normal hydrogen electrode (ENH);
- an auxiliary electrode for platinum type TM020 from Radiometer analytical brand with a large surface area through which passes the electric current necessary to produce the desired potential difference;
- an arrival of argon for the solution bubbling.

Methods

The supporting electrolyte used is a solution of 0.1 M KCl dissolved in 0.02 M acetic acid-sodium acetate buffer at pH 5. The analysis of the anodic dissolution solutions is preceded by that of

the support electrolyte then preliminary experiments on standard solutions of sodium molybdates ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) dissolved in the support electrolyte in order to establish the electroactivity range of molybdate ions. Before any measurement, the pH of the test sample is adjusted to 5 in order to have in solution all the dissolved forms of molybdenum (VI) which are reducible on glassy carbon. The oxygen dissolved in the solution is removed by bubbling away with argon for 10 min. Solutions are prepared on the day of the experiment. For the quantitative study of the solutions, cyclic voltammetry in anodic redissolution coupled with the metered addition technique was used in this work.

Study of Standard Molybdate Ion Solutions

A stock solution of MoO_4^{2-} (10^{-3} M) molybdate ions is prepared by dissolving the corresponding amount of sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) in the supporting electrolyte. Solutions of lower concentrations between 10^{-3} and 10^{-6} M are obtained by diluting the stock solution with the electrolyte. A pre-electrolysis is carried out at a constant potential of 200 mV for 2 minutes. Then a linear round trip potential scan is performed from 0 to -1000 mV/Ag.

Study of Anodic Dissolution Solutions

Dissolution of the MoSe_2 material was carried out in a basic media (1 M KOH), the electrode being subjected to a potential of 1.2 volts for 24 hours. The solution thus obtained is a solution for dissolving the anodic material MoSe_2 in the electrolytic media.

1 mL of this solution is taken, which is diluted 10 times with the supporting electrolyte (0.1 M KCl + 0.02M acetic acid-sodium acetate buffer). The test portion is analyzed by cyclic voltammetry using as the working electrode a rotating disk electrode with a glassy carbon tip using the anodic redissolution technique. The method consists in carrying out, for 2 minutes, a pre-electrolysis at constant potential of 2 mV and corresponding to the diffusion plateau so that there is reduction of the molybdate ions.

Once the pre-electrolysis is complete, the metal deposited on the surface of the electrode is redissolved by anodic oxidation by performing a linear return scan of potential from -1000 mV to 0 mV (same conditions as the standard solutions).

RESULTS AND DISCUSSIONS

Study of Standard Molybdate Ion Solutions

Study of a Standard Solution of Molybdate Ions as a Function of the concentration

Figure 1 shows the voltammograms obtained by analysis of the support electrolyte and standard solutions of molybdate ions of various concentrations. These solutions were obtained by successive additions of 40 μL of the stock solution (10^{-3} M) to the support electrolyte. We note the presence of a reduction peak towards -0.790 V, the height of which increases with the addition.

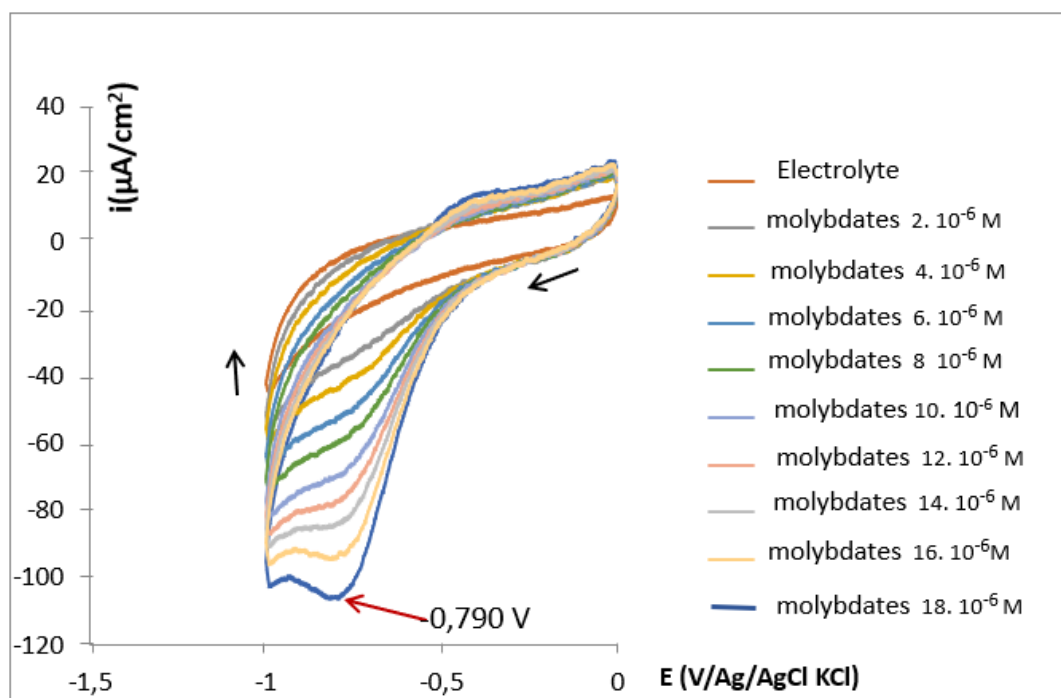


Figure 1. Voltammograms of standard solutions of molybdate ions in KCl (0.1 M) + acetic acid-sodium acetate buffer; round trip scanning from 0 to -1000 mV at a speed of 50 mV/s : study as a function of the concentration (C)

The reduction peak current values are determined by choosing a baseline against which to measure the respective heights of each peak. The proportionality between the peak current and the concentration of the standard solutions was verified by plotting the curve of the variation of the current intensity of the reduction peaks as a function of the concentration of the standard solutions (Figure 2). It can be seen that the curve obtained is linear with a correlation coefficient equal to 0.993. This proves that the working electrode is well suited for this study.

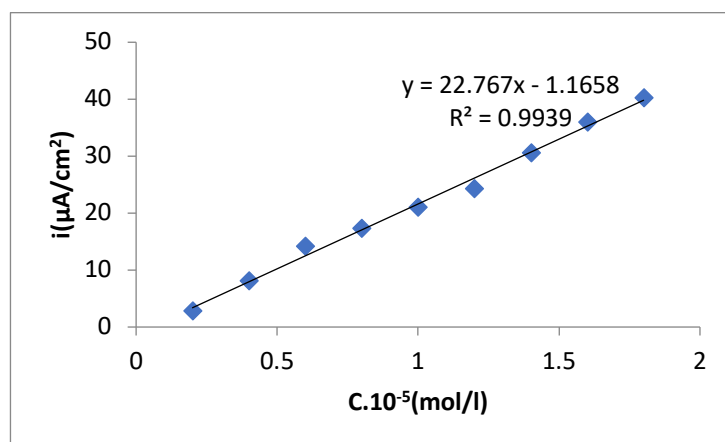


Figure 2. Calibration curve $i = f(C)$ of the working electrode

Study of a Standard Solution of Molybdate Ions as a Function of the Scanning Speed

Figure 3 shows the voltammograms obtained by analysis of a standard solution of molybdate ions (6.54×10^{-5} M) as a function of the scanning speed. This solution was obtained by adding

1.4 mL of the stock solution (10^{-3} M) to the supporting electrolyte. Note that the voltammograms have the same characteristics. Indeed, we observe the presence of a reduction peak towards -0.790 V indicating the deposition during the pre-electrolysis. A first oxidation peak at around -0.740 V and a secondary peak at around -0.429 V. Both peaks are significant and correspond to the oxidation of the deposit during anodic redissolution. The shape of the voltammograms obtained in the standard solutions allows a better interpretation of the voltammograms of the anodic dissolution solutions.

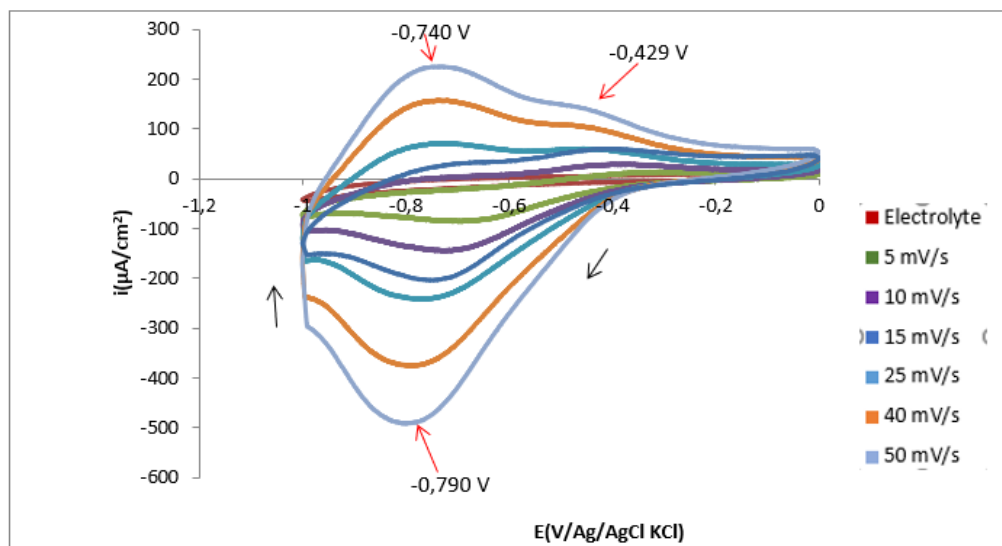


Figure 3. Voltammograms of a standard solution of molybdate ions (6.54×10^{-5} M) in KCl (0.1 M) + acetic acid-sodium acetate buffer (0.02 M). Scanning from 0 to -1000 mV : study as a function of the scanning speed

The reduction peak current values recorded by measuring the height of each peak were used to plot the curve of the variation of the peak current intensity as a function of the scanning speed (Figure 4). The linearity of the curve indicates on the one hand that the current of the reduction peaks is proportional to the scanning speed. On the other hand, it indicates that the phenomena take place on the surface of the electrode [19].

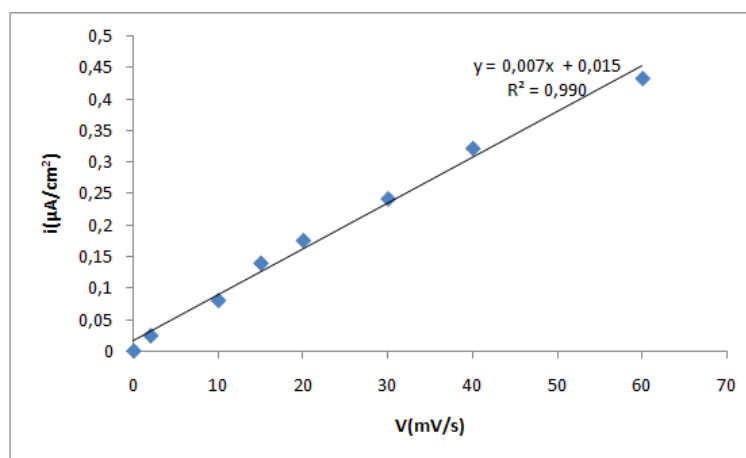
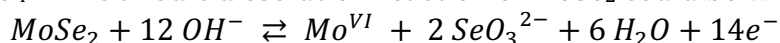


Figure 4. Curve of variation of the current intensity of the reduction peaks as a function of the scanning speed; $i = f(v)$

Study of the Anodic Dissolution Solutions of MoSe₂ in KOH Media

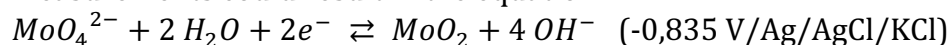
After studying the standard solutions and developing the method, the analysis of the anodic dissolution solutions in KOH media was carried out. The voltammograms obtained by analysis of the anodic dissolution solutions in KOH media (1 M) and standard solutions of sodium molybdates (Na₂MoO₄) of various concentrations are presented in figure 5. These voltammograms have the same characteristics. In fact, a first significant oxidation peak is observed at about -0.740 V and a secondary oxidation peak at around -0.429 V. These two peaks are sufficiently defined attesting to the presence of a deposit during pre-electrolysis which oxidizes during anodic redissolution.

The literature [20] specifies that the dissolution of MoSe₂ occurs at high polarizations (1.2 V) and corresponds to the passage of the metal (Mo) in the form of an ion of oxidation degree +VI in the solution. More, molybdenum dissolves in the hexavalent state (Mo^{VI+}) by anodic polarization in solutions of HCl, KOH and neutral salt [21]. This particular behavior of molybdenum is in accordance with the diagram of Pourbaix [22] where in an alkaline media, the metal is covered with an oxide film and dissolves in molybdate ions MoO₄²⁻, while in an acid media, it is likely to first dissolve into molybdenous Mo³⁺ ions at relatively low electrode voltages and become covered with a passivating layer of MoO₂ or MoO₃. We can therefore conclude that during the dissolution of MoSe₂ by anodic attack of 1.2 volts for 24 hours in 1M KOH, the molybdenum is mainly dissolved in the form of ions of oxidation degree +VI and would be in the form MoO₄²⁻. The anodic dissolution reaction of MoSe₂ could be written:



The reduction peak around -0.835 V/Ag/AgCl/KCl (3M) can be attributed to the reduction of molybdenum (VI) to molybdenum (IV) MoO₂ which initially forms on the surface of the electrode during the pre-electrolysis. Then the anodic redissolution of the molybdenum (IV) MoO₂ is done with recording of the oxidation peak at -0.740V.

The reduction reaction taking place at the working electrode during voltammetry measurements could result in the equation:



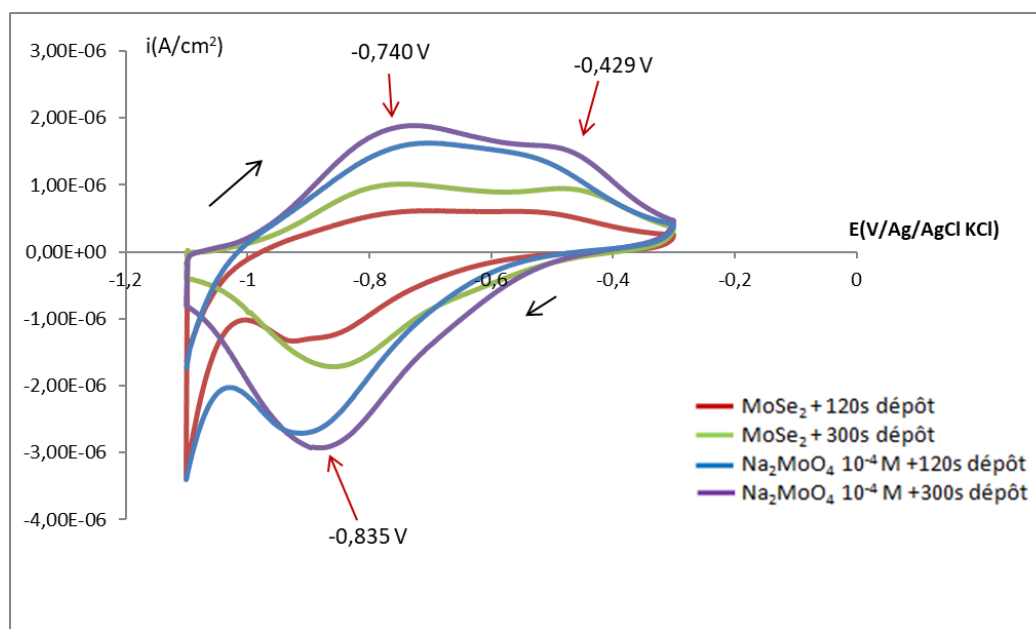


Figure 5: Voltamograms of the anodic dissolving solution of MoSe₂ in KOH medium (1M) and of standard Na₂MoO₄ solution in the presence of supporting electrolyte KCl 0,1M + 0.02M acetic acid-sodium acetate buffer

CONCLUSION

The study of the behavior of the MoSe₂ semiconductor by anodic dissolution at fixed potential during 24 hours in an electrolytic media has been performed. Study of standard solutions of molybdate ions made it possible to establish the electroactivity range of molybdate ions. The behavior of the material MoSe₂ in the basic media has been determined. Analysis of the anodic dissolution solutions obtained by anodic attack in KOH (1M) shows that MoSe₂ is not stable in a basic media; it dissolves according to an anodic decomposition process. This result can be put to good use in recovering the molybdenum contained in solar cells after attacking the material in a basic medium and then depositing it on a glassy carbon electrode.

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