Study on Electrochemistry of Composite Electrode of Nano Reticular MoS$_2$/RuO$_2$

Yun Lu, Jiancheng Ke, Wei Wang, Ruolan Wang, Li Wang

School of Electronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu 610054, China

Abstract. Nano Reticular MoS$_2$ is prepared in the hydrothermal method. By means of hydrothermal method, the cathode material of composite electrode of MoS$_2$/RuO$_2$ is prepared. For all kinds of prepared samples, physical characterization analysis, such as SEM and XRD, and electrochemistry tests, such as cyclic voltammetry, alternating-current impedance and galvanostatic charge-discharge, are conducted. The test results show that the addition of a small amount of molybdenum disulfide improves the specific capacity of composite electrode, lowers alternating equivalent impedance and improves conservation ratio of specific capacity. When the doping content of molybdenum disulfide is 25%, specific capacity of binary composite electrode can reach 413 F/g and equivalent alternating-current impedance is equal to 0.665 Ω. By means of 800 charge-discharge cycles, specific capacity still remains around 87%. Key words: Molybdenum Disulfide; Hydrothermal Method; Binary Composite Electrode Materials; Equivalent Alternating-current Impedance; Specific Capacity.

In recent years, most researches focus on improving the energy production and the performance of storage device. The super capacitor is considered to be a very promising power storage device and compared with similar power storage device, has superior performance, which means battery. Different from batteries, charging and discharging process of super capacitors is faster. Compared with batteries, it has higher power density and longer service life [1]. In the next several years, it can play more important role in energy storage field. Super capacitors of transition metal oxides, such as Sn, Mn, Ti, Co, and Ru, are explored to be applied to this application [2-5]. Transition metal oxides, such as RuO$_2$, have high theoretical specific capacity, but have poor conductive property, poor cycling stability and other shortcomings, which have limited its application.

Due to high surface volume ratio and surface charge ratio, two-dimension nano materials have attracted the interests of researchers with its unique physical, chemical and biological functions. From the perspective of crystallography, two-dimensional crystals commonly have highly anisotropic physical property [6-9]. Molybdenum disulfide has the merits, such as less gathering, larger than superficial area, network interconnection and vertical channels' effectively exposing active sites. Molybdenum disulfide is an important 2D material and the supplementary material of graphene and is very attractive. MoS$_2$ has the merits, such as compared with superficial area, larger area, good chemical stability, high ionic conductivity and laminated structure, and has certain advantages in electrochemical devices [10, 11]. Intrinsic ionic conductivity is higher than the one of oxides. Theoretical capacitance is higher than graphite specific conductance [12-14]. Excellent storage capacitance makes it have multitudes of excellent mechanical, optical and electronic performance and has it applied in many electronic circuits,
which need low standby power, as well as effective photocatalysis, solar energy funnel, electronics and excitonic integrated circuit [15, 16]. In the semiconductor prepared by MoS$_2$, it can be observed the change from indirect band gap type to direct band gap type [17, 18].

Molybdenum disulfide has these merits, such as less gathering, compared with superficial area, lager area, network interconnection, vertical channels’ effectively exposing active sites. Transition metal -- ruthenium oxide has the features, such as high specific capacity, easy agglomeration and poor cycling performance. This article has prepared reticular nano molybdenum disulfide/RuO$_2$ composite electrode material and improved the shortcoming of ruthenium oxide by using the advantage of molybdenum disulfide, which is not easily condensed, and then further improved the performance of composite electrode material.

1. Experiment

1.1. Preparation of MoS$_2$
Weigh appropriate amount of high-purity molybdenum powder and disperse it into the deionized water (50ml); add in appropriate hydrogen peroxide and drip dispersion liquid of molybdenum trioxide into thiourea solution; mix it with magnetic force for 60 min, disperse it with the ultrasound of ultrasonic wave for 30 min, transfer the mixed solution into high pressure reactor (100ml) and seal it. And then put it into the constant temperature drying box (200℃) for about 10 hours and cool it till the room temperature. Filter the solution in the reactor and clean it with deionized water and absolute ethyl alcohol. Put the product after being filtered into the vacuum (80℃) to dry for a whole day. In the end, the reticular nano molybdenum disulfide can be achieved.

1.2. Synthesis of MoS$_2$/RuO$_2$ Composite Electrode Material
Weigh RuCl$_3$.H$_2$O (2.7g) and dissolve it in water (100ml). Add in appropriate amount of nano molybdenum disulfide into it. Stir it with magnetic stirrer for 30 min and conduct the ultrasonic dispersion for 30 min. Pour the mixed liquors of RuCl$_3$/MoS$_2$ into the high-pressure reactor under normal pressure and around 200℃. After 12hours, it can be naturally cooled till room temperature. And then repeatedly wash it with deionized water and ethyl alcohol. In the end, put the product into the vacuum drying box (150℃) to dry for 10 hours.

1.3. Preparation of Composite Electrode
Weigh polyvinylidene fluoride (0.020g) and dissolve it in NMP solution (1.5g). Stir it with magnetic stirrers till it is transparent. Weigh mixed composite material of MoS$_2$/RuO$_2$ (0.16g) and mix it with conductive additive - acetylene black (0.02g). Add the mixed materials into the NMP solution mixed in polyvinylidene fluoride and sufficiently mix it till the proper viscosity. Use the applicator to evenly apply electrode slurry onto the tantalum sheet, which is handled properly. And then put the tantalum sheet into the vacuum drying box (60℃) to dry for 6 hours, then dry for 8 hours under the temperature of 110℃, as well as dry for 3 hours under the temperature of 170℃. Then composite electrode is achieved.

1.4. Testing Instruments
Use the JSM-6490LV Scanning Electron Microscope from JEOL, D8 ADVANCEX ray diffractometer from Rigaku Industrial Corporation, CS2350 double-cell electro-chemical workstation from Wuhan Corrtest Instruments Corporation and CT2001A super-capacitor test system from Wuhan LAND Electronic Co., Ltd. The test process is completed under room temperature.
2. Results and Discussion

2.1. Scanning Electron Microscopy (SEM) Analysis
Figure (a) is the nano ruthenium oxide synthesized by liquid phase precipitation method. It is globular aggregation and arrangement among ruthenium oxide. Figure (b) is the reticular nano molybdenum disulfide, which is produced by using high-purity molybdenum powder and thiourea under hydrothermal reaction. Figure (c) is composite electrode material prepared by hydrothermal method of MoS$_2$/RuO$_2$. From the figure, we can see clearly that reticular nano molybdenum disulfide can be better embedded in ruthenium oxide, which is accumulated and arranged. Figure (d) is EDS chart of composite electrode material of MoS$_2$/RuO$_2$. From the figure, we can see the main components of composite electrode material are the elements -- O, Mo and Ru.

![SEM Images](image1)

**Figure 1. XRD and EDS of Electrode Material**
(a) XRD of Granular Ruthenium Oxide Synthesized by Liquid Precipitation Method; (b) XRD of Reticular Nano Molybdenum Disulfide Generated by High-purity Molybdenum Powder and Thiourea under Hydrothermal Reaction; (c) XRD of Composite Electrode Materials of MoS$_2$/RuO$_2$; (d) EDS of Composite Electrode Materials of MoS$_2$/RuO$_2$

2.2. XRD Analysis

![XRD Chart](image2)

**Figure 2. XRD Diffraction Pattern of Composite Materials of MoS$_2$/RuO$_2$ Prepared and Synthesized with Hydrothermal Method**
Figure 2 is XRD of composite electrode materials of MoS\(_2/RuO_2\). In the figure, 14.2°, 33.2°, 39.6° and 59° are the diffraction peaks of MoS\(_2\), which respectively respond to crystal faces of (002), (100), (103) and (110) of MoS\(_2\). 34.51°, 50.76° and 62.5° are the crystal faces of (101), (211) and (310) of RuO\(_2\). In the figure, the diffraction peak at 14.2° is very pointed. The diffraction peak corresponds to 14.2° of MoS\(_2\), which means along the direction of C axis, reticular nanostructure is good. At the same time, at 39.6° of diffraction peak, it respectively corresponds to the crystal face of (103) of MoS\(_2\). MoS\(_2\) is better embedded in RuO\(_2\), which is accumulated.

2.3. Cyclic Voltammetry Features

The electrode materials are performed the test of electrochemical cycling performance. The electrolytic tank is put in 38% sulfuric acid solution, Pt electrode is applied for the auxiliary electrode, mercury - mercurous sulfate electrode is applied for reference electrode (saturated K\(_2\)SO\(_4\)). From the figure, it can be clearly seen that composite electrode material of MoS\(_2/RuO_2\) has very good pseudocapacitance feature. From the figure, we can see with the improvement of the content of molybdenum disulfide, the area of rectangle presents the trend of increasing first and reducing later. And rectangle area is the representation of material specific capacity. When the content of molybdenum disulfide is 25%, the area of rectangle is the largest. When the content of molybdenum disulfide is within the range from 0% to 25%, specific capacity presents the trend of improvement. Because laminated molybdenum disulfide is embedded in the accumulated ruthenium oxide, it makes the superficial area of composite electrode larger and improves specific conductance, and then further improves specific capacity. And when the content of molybdenum disulfide keeps improving, specific capacity of electrode material presents the trend of declining. The reason is that the content of molybdenum disulfide improves, and correspondingly, the content of ruthenium oxide is reduced. And the feature of pseudocapacitance is also reduced.

![Figure 3](image-url)

**Figure 3.** Cyclic Voltammetry Features of Composite Electrode of MoS\(_2/RuO_2\) under different contents of MoS\(_2\) (10mV/s)

2.4. Measurement of Specific Capacitance

For the computational formula of specific capacitance, refer to formula 1. Thereof, \(I\) is the discharge current (unit: A), \(\triangle t\) is the discharge time (unit: s), \(m\) is the electrode material quality (unit: g), \(\triangle V\) is the voltage range and \(C\) is the capacity of supercapacitor (unit: F/g)

\[
C = \frac{I\triangle t}{m\triangle V}\tag{1}
\]

Figure 4 is the charge-discharge curve of current under different contents of MoS\(_2\). Discharge current is 50mA/cm\(^2\), electrolysis is the sulfuric acid solution, with the concentration of 38%. The voltage range of charge-discharge is 0 ~ 1 V. Table 1 is the discharge time and specific capacity under different concentrations of MoS\(_2\).
Figure 4. Galvanostatic Charge-Discharge Curve of Composite Electrode of MoS$_2$/RuO$_2$ under Different Contents of MoS$_2$

| MoS$_2$ content | 0%  | 15% | 25% | 35% | 45% |
|-----------------|-----|-----|-----|-----|-----|
| Discharge time(s) | 326s | 393s | 478s | 356s | 273s |
| Specific capacitance (F/g) | 282 | 340 | 413 | 308 | 236 |

2.5. AC Impedance Features
Figure 5 sees AC equivalent impedance of electrode materials under different contents of MoS$_2$. AC equivalent impedances under 0%, 15%, 25%, 35% and 45% are respectively 0.934Ω, 0.864Ω, 0.665Ω, 0.64Ω and 0.358Ω. From the figure and data, we can see when MoS$_2$ is added in, AC equivalent impedance is reduced constantly. The reason is nanometer MoS$_2$ is embedded in globose ruthenium oxide, which has piled and arranged. This improves the electric conductivity among ruthenium oxide and then further improves resistance properties.

Figure 5. Electrochemical Impedance Spectroscopy of Composite Electrode of MoS$_2$/RuO$_2$ under Different Contents of MoS$_2$

2.6. Cycle Life
Cycle performance of composite electrode materials is the important index of the service life of supercapacitor, which makes the measurement system of LAND battery have the cycle performance of charging for 800 times under the voltage range of 0–1V and charge-discharge current density of 50mA/cm$^2$. 

**Figure 6.** The Curve of Specific Capacitance with the Number of Charges and Discharges

From the figure, we can see that under 0% content of MoS$_2$, with more charge-discharge times, the specific capacity of electrode material largely declines. The reason is although the transition metal - ruthenium oxide has higher specific capacity, agglomeration leads to poor dispersity and then further leads to the fast decline of ruthenium oxide capacity. From the figure, the content of MoS$_2$ is improved, which can improve the cycle performance of ruthenium oxide and the conservation rate of specific capacitance. The reason is reticular nano - molybdenum disulfide has the merits, such as less gathering, larger area (compared with superficial area), network interconnection, vertical channels' effectively exposing active sites, which make up for the shortcoming that agglomeration of transit metal leads to poor cycle performance.

| MoS$_2$ content | 0%     | 15%    | 25%    | 35%    | 45%    |
|----------------|--------|--------|--------|--------|--------|
| Conversation Rate of Specific Capacitance (%) | 75.2%  | 82.6%  | 87.1%  | 88.5%  | 91.5%  |

3. Conclusion

(1) The addition of reticular nanometer molybdenum disulfide enlarges the superficial area of MoS$_2$/RuO$_2$ and improves specific conductance. Under the electric current density of 50mA/cm$^2$, specific capacity is improved to 413F/g and impedance is reduced to less than 0.665Ω.

(2) By means of 800 times galvanostatic charge-discharge, specific capacity of composite electrode of MoS$_2$/RuO$_2$ remains around 87%.

(3) By utilizing the merits of reticular nanometer molybdenum disulfide—difficult agglomeration, larger area (compared with superficial area) and high ionic conductivity, the composite electrode materials of MoS$_2$/RuO$_2$ synthesized can effectively improve pseudocapacitance feature of ruthenium oxide.

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