Electrochemical Performance of Molybdenum Disulfide Supercapacitor Electrode in Potassium Hydroxide and Sodium Sulfate Electrolytes

Raja Noor Amalina Raja Seman, Mohd Asyadi Azam, Mohd Fareezuan Abdul Aziz , Raja Izamshah, Mohd Shahir Kasim

Abstract*: Two-dimensional materials have attracted growing interest in research because of their specific electronic, physical, optical and mechanical properties. Molybdenum disulfide was theoretically investigated as novel energy storage materials because of its unusual physicochemical properties. This paper describes easy approach to fabricate molybdenum disulfide (MoS_2) electrode using slurry technique on conducting substrate namely Ni foam as current collector for supercapacitor device application. This MoS_2 electrode exhibits relatively good specific gravimetric capacitance, (C_{sp}) of 11.12 to 12.38 Fg^{-1} at 1 mVs^{-1} scan rate. Moreover, galvanostatic charge-discharge displays symmetrical triangular curves which attributed to the fast charge-discharge process (in seconds). These results show that MoS_2 active material can be charged and discharged reversibly between 0.2 and 1.0 V (in 6 M KOH) and between 0.3 and 1.0 V (in 0.5 M Na_2SO_4). From cyclic stability test exhibits capacitance retention of up to 83% and 64% after 1000 cycles in 6 M KOH and 0.5 M Na_2SO_4, respectively. The MoS_2 electrode is thus a promising material for future application of the supercapacitor.

***Keywords*: Aqueous electrolytes, Electrochemical performance, Molybdenum disulfide, Supercapacitor**

I. INTRODUCTION

Over the past few years, numerous studies have been explored in the two-dimensional (2D) structures including graphene due to their outstanding properties related with their atomic-layer thickness and 2D morphology [1,2]. Instead of graphene as 2D material, the discovery and concentration of other kinds of 2D nanomaterials is now directed to the nanostructures of transition metal dichalcogenides [3,4]. Molybdenum disulfide (MoS_2) is composed of S- Mo-S whereby at each layer, atoms are stacked together by covalently bonded and each individual layers are bonded via van der Waals effect [5]. This bonding may be inferred from its dimensional structure, similar to some carbon nanomaterials [6]. MoS_2 has been extensively considered and exhibited many appealing features [7] for various applications such as electronics, optoelectronics [8], supercapacitors, batteries [9], hydrogen evolution reaction [10], sensors [11], and so on. There are several methods to synthesize MoS_2, such as electrochemical lithium intercalation and exfoliation, direct sonication in solvents, and chemical vapor deposition [12-15]. Generally, there are three types of electrolytes that usually used in supercapacitor such as aqueous electrolyte, organic electrolyte, and ionic liquids [16]. Some examples including potassium hydroxide, sodium sulphate, and sulfuric acid are the most commonly studied aqueous electrolytes for supercapacitors [17] due to their low toxicity and low cost [18]. Also, not to forget the ability of aqueous solutions to provide higher ionic concentration and lower resistance as compared to organic electrolytes. Herein, we present a facile fabrication of MoS_2 electrode by using conventional slurry technique. The electrochemical performances of MoS_2-based supercapacitors in alkaline and neutral aqueous electrolytes were studied.

II. EXPERIMENTAL

A. Preparation of MoS_2 Electrode

For the fabrication of the MoS_2 electrode, the active material shall be prepared for purposes including electrochemical testing. First, the slurry was prepared. The electroactive material which is commercially available MoS_2 powder, super-P and poly(tetrafluoroethylene) (PTFE) were mixed well in weight ratios of 80:10:10. Nickel foam was used as current collector. The slurry was coated onto roundly-cut nickel foam and then dried at 100°C for 12 h. For the assembly of a symmetric supercapacitor, the active material's average mass was estimated to be approximately 10 mg. Fig. 1 summarizes the experimental flow to fabricate the MoS_2 electrode.

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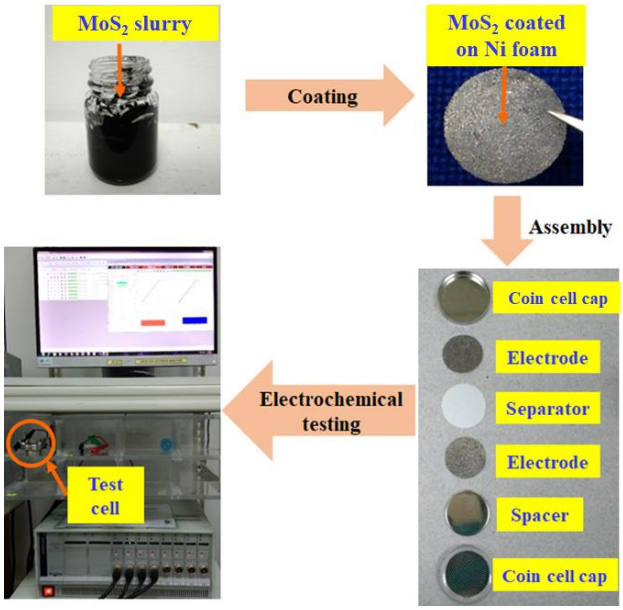

Fig. 1. The experimental flow for the fabrication and testing of MoS_2 electrode.

B. Electrochemical Measurement

Supercapacitive properties of the MoS_2 electrode were measured in a three-electrode cell configuration; MoS_2 electrode as working electrode, Ag/AgCl (3 M KCl) solution as reference electrode, and a platinum rod as counter electrode. The electrochemical measurements were carried out by using WonAtech electrochemical workstation. Also, the electrochemical output of the electrode was elaborated with 6 M potassium hydroxide (KOH) and 0.5 M sodium sulphate (Na_2SO_4) aqueous electrolytes.

III. RESULTS AND DISCUSSION

A. Cyclic Voltammetry Analysis

Cyclic voltammetry (CV) study was performed in a three-electrode configuration to determine the electrochemical efficiency of MoS2 as the active material for the supercapacitor electrode. Fig. 2 shows the CV curves of MoS_2 supercapacitors at various scan rates in 6 M KOH and 0.5 M Na_2SO_4 aqueous electrolytes. Fig. 2a shows the CV curves of the prepared electrodes at different scan rates ranging from 20 to 80 mV s^{-1} in the 6 M KOH electrolyte. The CV of MoS_2 electrode was found to have quasi-rectangular without a redox peak, which confirmed a typical electrical double-layer capacitor (EDLC). The shape of the CV curves were retained up to 80 mV s^{-1} and this reveals a good high-scan-rate capacitive performance of the MoS_2 electrode [19,20]. In addition, the electrochemical performance of MoS_2 electrode in 0.5 M Na_2SO_4 aqueous electrolyte (Fig. 2b) was studied. These MoS_2-based supercapacitors were tested with two different electrolytes commonly used in commercial EDLCs [21]. Aqueous electrolytes including KOH, H_2SO_4, and Na_2SO_4, can provide a lower resistance and higher ionic concentration compared with organic electrolyte. This may be due to smaller ionic radius and higher ionic concentration of aqueous electrolytes compared with organic electrolytes. Instead of organic electrolyte which needs a stringent processes and safety conditions to prepare the electrolyte, aqueous electrolytes were easily prepared and can be used without a need of a strict control of the preparing processes and conditions [16]. The specific gravimetric capacitance, C_{sp} of the MoS_2 electrode was calculated using the integration of voltammetric charge from the CV and following the equation in below;

$$Csp = \frac{\int_{E1}^{E2} i(E)dE}{2(E2 - E1)mv} \quad (1)$$

where E1 and E2 are the potentials in CV. *i(E)* is the current. $\int_{E1}^{E2} i(E)dE$ is the integral area enclosed by the CV, *m* is the electrode's average mass and *v* is the scan rate [22].

The C_{sp} was calculated from the electrode material used, meanwhile the potential window is based on the electrolyte used [23]. In this work, the operating window for MoS_2-based supercapacitor in 6 M KOH and 0.5 M Na_2SO_4 ranging from 0.2 to 1.0V and 0.3 to 1.0, respectively. The C_{sp} values calculated for the MoS_2-based supercapacitors in 6 M KOH and 0.5 M Na_2SO_4 are 12.38 and 11.12 F g^{-1}, respectively. The result obtained may be due to the low intrinsic electrical conductivity of the active material. Also, the restacking of MoS_2 sheets by van der Waals remains a major obstacle for supercapacitors to use as electrodes [24]. In addition, a low C_{sp} may be attributed from the low conductivity of the MoS_2 molybdenite phase [20]. In 6M KOH, the CV curve showed slightly distorted rectangular shape resulted from the typical EDLC behavior dominated the charge-discharge process. On the other hand, the MoS_2-based supercapacitor in 0.5 M Na_2SO_4 has a much higher current compared with CV curves in 6 M KOH, owing to the EDLC contribution from MoS_2 [25]. The EDLC storage mechanism of MoS_2-based supercapacitor can be explained as follows; the electrode surfaces produce excess electrical charges, and electrolyte ions are built up on the electrolyte side to achieve electro-neutrality which happens on the electrode-electrolyte interfaces. When charging, the electrons pass through an external charge from the negative to the positive electrode. Anions and cations in electrolyte were move towards positive and negative electrode, respectively. For discharging, the process is vice versa. Based on the MoS_2 supercapacitor, there is no charge transfer between MoS_2 electrode and electrolyte interface. This indicates that during the cycle of charging and discharging, the electrolyte concentration remains constant. The electrical energy is stored in the interface of the double layer [16] and the C_{sp} decreases with increasing the scan rate. The efficiency of electrodes decreases at higher scan rates because the internal active sites of the electroactive material are relatively inaccessible to the electrolyte ions [26].

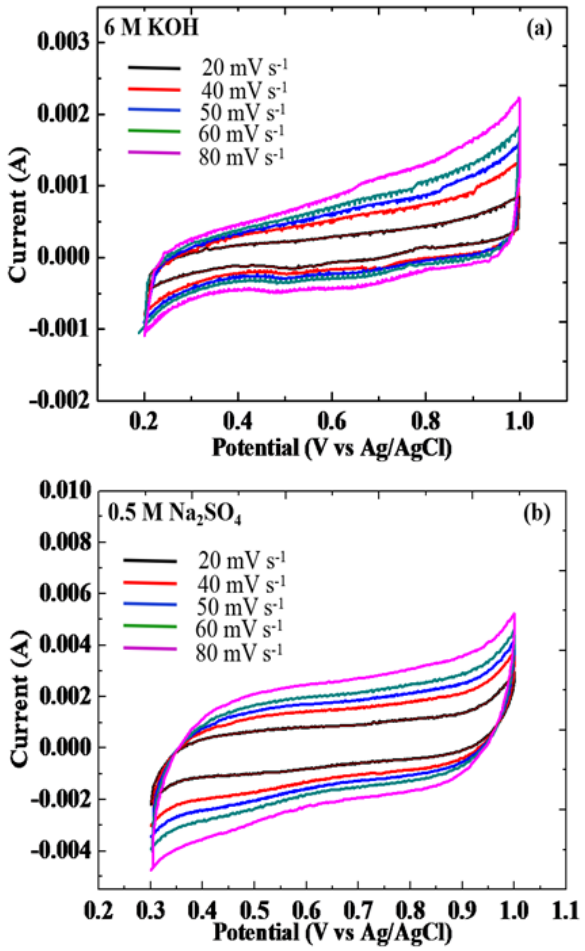

Fig. 2. CV curves for MoS_2-based supercapacitors at various scan rates (20, 40, 50, 60, and 80 mV s^{-1}) in (a) 6 M KOH and (b) 0.5 M Na_2SO_4 aqueous electrolytes.

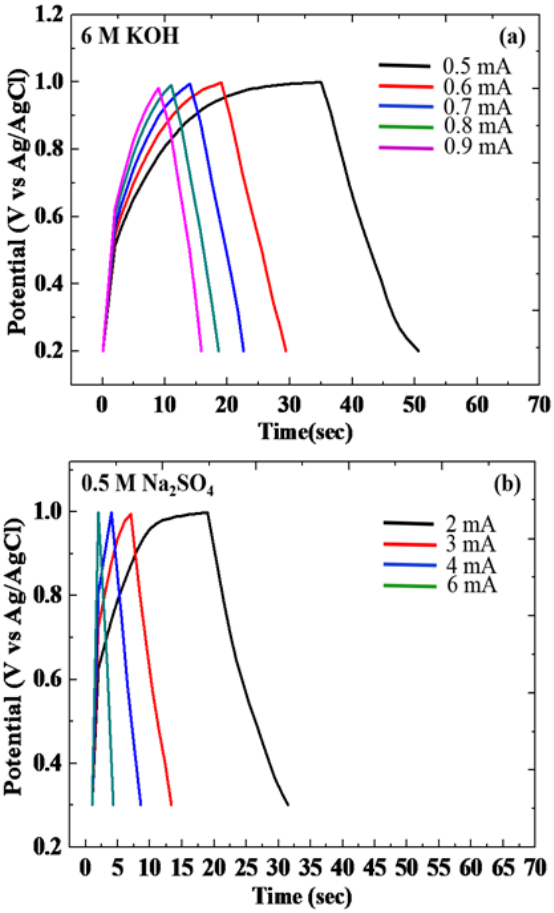

Fig. 3. Galvanostatic charge-discharge curves of MoS_2 electrodes at various currents in (a) 6 M KOH (0.5, 0.6, 0.7, 0.8, and 0.9 mA) and (b) 0.5 M Na_2SO_4 (2, 3, 4, and 6 mA) aqueous electrolytes.

B. Galvanostatic Charge-Discharge

Fig. 3 shows the galvanostatic charge-discharge (GCD) plots of the MoS_2 supercapacitor electrode at charge-discharge currents ranging from 0.5 to 6 mA. The GCD slopes of MoS_2 in 6 M KOH at different currents are within the potential window of 0.2-1.0V, while the MoS_2 electrode in 0.5 M Na_2SO_4 at different currents are within the potential window of 0.3-1.0V. The charging behavior is almost linear and in symmetry to the discharge one, which also shows the good reversible reaction and higher current efficiency of MoS_2 electrodes [20,26]. The C_{sp} values obtained from the GCD curves are following equation (2) in below:

$$Csp = \frac{2I}{m(\frac{dV}{dt})} \quad (2)$$

where I is the current, m is the electrode's average mass of the active material in each electrode and dV is the charge/discharge potential window (V) and dt is the discharge time (sec) [27].

The C_{sp} of MoS_2 in 6 M KOH are 2.544, 2.103, and 2.084 F g^{-1} at the currents of 0.5, 0.6, and 0.7 mA respectively. The corresponding C_{sp} of MoS_2 in 0.5 M Na_2SO_4 are 7.013, 5.591, and 5.478 F g^{-1} at the currents of 2, 3, and 4 mA, respectively. The C_{sp} decreases with the increasing discharge current. This is suggested could be due to the electrolyte ion hindered from penetrating into the MoS_2 electrode pores [26].

C. Cyclic stability analysis

The cyclic property of the electrode was also assessed and discussed in this section. The electrochemical stability of the MoS_2 electrodes was investigated at 1 mA and 7 mA currents in 6 M KOH and 0.5 M Na_2SO_4 aqueous solutions, respectively. Fig. 4 depicts the capacitance retention (in %) of MoS_2 electrode as a function of cycle number. The result revealed a relatively good and stable electrochemical behaviour with 83% and 64% retention after 1000 cycles in 6 M KOH and 0.5 M Na_2SO_4 electrolytes, respectively. Other than the just nice ion size of the KOH electrolyte, this is also suggested due to the porous and hierarchical MoS_2 nanostructures. It increases the surface area with more active sites and quickly penetrates the electrolyte ions into the MoS_2 structure. In addition, the good performance of MoS_2 electrode may be due to the good electrical conductivity between MoS_2 nanostructures and the current collector [26]. The cyclic stability of the MoS_2 may be attributed from the contribution of double-layer at the surface-interface sites. Instead of pseudocapacitance which related to a chemical process, the double-layer mechanism involves only a charge rearrangement and has greater electrochemical stability but a decreased specific capacitance. Although two-electrode cell construction is recommended for a real market of energy storage devices including supercapacitor, the three-electrode cell measurement used is still acceptable for material chemistry investigation [28].

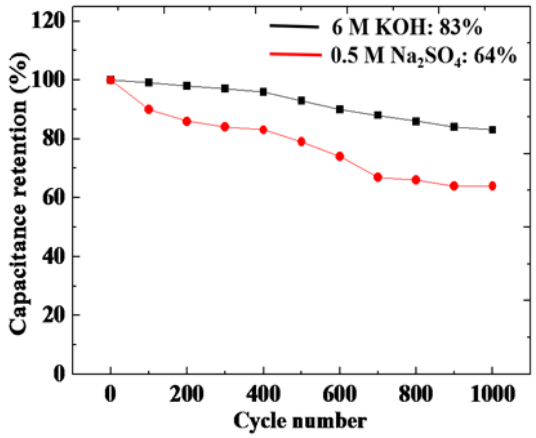

Fig. 4. Cyclic performance of the MoS_2-based electrode at 1mA and 7mA in 6 M KOH and 0.5 M Na_2SO_4 aqueous electrolytes.

IV. CONCLUSION

This paper describes easy approach to fabricate molybdenum disulfide (MoS_2) electrode using slurry technique on conducting substrate namely Ni foam as current collector for supercapacitor device application. Supercapacitor based on MoS_2 was successfully assembled by slurry preparation to construct the electrode. The MoS_2 electrodes showed relatively an acceptable capacitive performance and good cyclic stability. From electrochemical testing, it was found that the MoS_2 electrode showed a good double layer behavior, linear symmetrical triangular charge-discharge curve, and good cyclic performance. The MoS_2 electrode has superior electrochemical efficiency; relatively good specific gravimetric capacitances (C_{sp}s) of 11.12 to 12.38 Fg^{-1} at 1 mVs^{-1} were obtained. Moreover, galvanostatic charge-discharge analysis gave symmetrical triangular curves which interpreted the fast charge-discharge process (in seconds). Cyclic stability test exhibits capacitance retention of up to 83% and 64% after 1000 cycles in 6 M KOH and 0.5 M Na_2SO_4, respectively. The good electrochemical performance may be attributed from the MoS_2 two-dimensional properties. Finally, it can beb concluded that MoS_2 is yet another promising source for supercapacitors'electrode.

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