

Synthesis, structure and electrochemical performance of MoO₂ /reduced graphene composites

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Introduction

Molybdenum dioxide is a promising electrode material for electrochemical energy storage devices. The possibility of a series of oxidation states of Mo ions from +2 to +6 in the surface redox reaction suggests high values of the theoretical specific capacitance of MoO₂ (about 838 mA g⁻¹), which exceeds the theoretical capacitance of graphite (about 372 mA g⁻¹). Another advantage is a correspondingly higher density (6.5 g / cm³ for MoO₂ compared to 2.3 g / cm³ for graphite), which implies a higher energy density for redox electrodes. The use of ultrafine and nanostructured MoO₂ suggests an increase in cycling ability by reducing ion diffusion pathways in combination with the electrode / electrolyte interface area. The formation of a composite based on ultrafine MoO₂ and carbon nanomaterials makes it possible to increase the pseudocapacitive performance due to synergistic effects in charge transfer mechanisms.

Experimental Details

Ultrafine MoO₂ and MoO₂ /rGO composites have been obtained by the hydrothermal method. Na₂MoO₄·2H₂O was dissolved in 50 ml of H₂O and 50 ml of ethanol to a concentration of 10 mmol. Colloidal graphene oxide (GO) synthesized by the modified Hummers' method was used as a component of the reaction media. The resulting mixture was hydrothermally treated at 160°C for 6 hours. Pure MoO₂ (sample S0), as well as two MoO₂/rGO samples with a mass ratio of oxide and graphene components of 2:1 and 1:1 (samples S05 and S10, respectively) have been prepared.

1 XRD

XRD patterns of pure MoO₂ (S0) and MoO₂ /rGO composite materials (S05 and S10) are shown in Fig.1. The monoclinic structure of MoO₂ (JCPDS 65-5787; space group P21/c) has been detected for all samples. Values of 5.2, 5.7 and 4.4 nm have been obtained for materials S0, S05 and S10 using Scherrer equation. The average thickness of the package of graphene planes for MoO₂ / rGO materials was 1.7 and 1.4 nm for samples S05 and S10, respectively (XRD data).

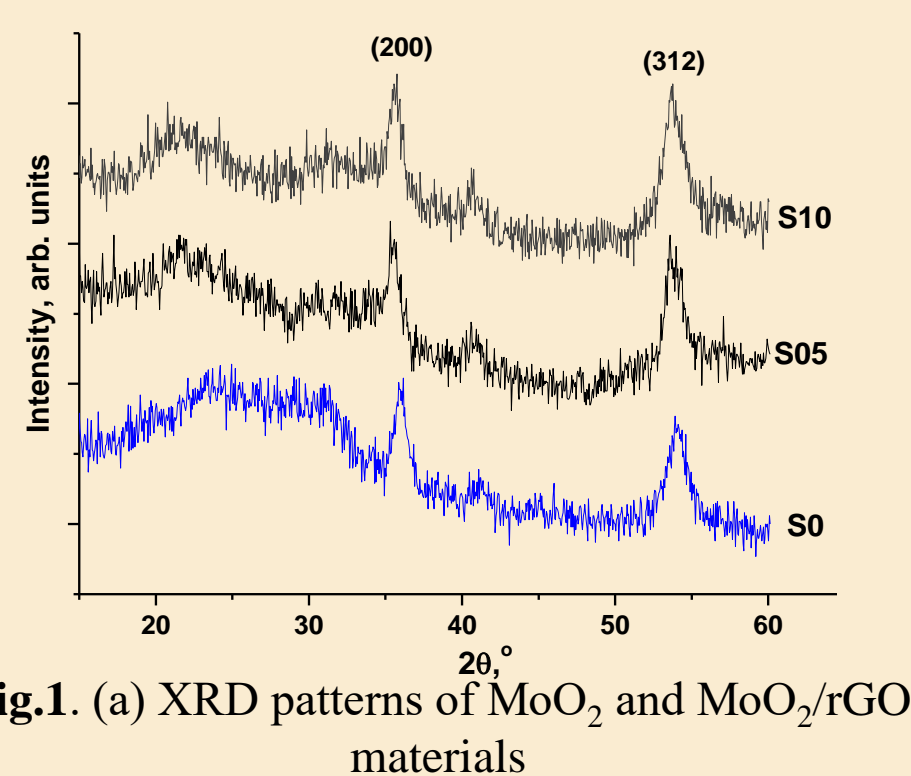


Fig.1. (a) XRD patterns of MoO₂ and MoO₂/rGO materials

2 Scanning electron microscope

The MoO₂ sample consists of spherical agglomerates with an average size of about 14-20 nm (Fig.2, a). The MoO₂ / rGO samples are characterized by comparatively smaller agglomerates of about 12-13 nm (Fig.2, b-c). The MoO₂ / rGO material is much more blurry, which can be explained by the formation of carbon shells (Fig.2, c).

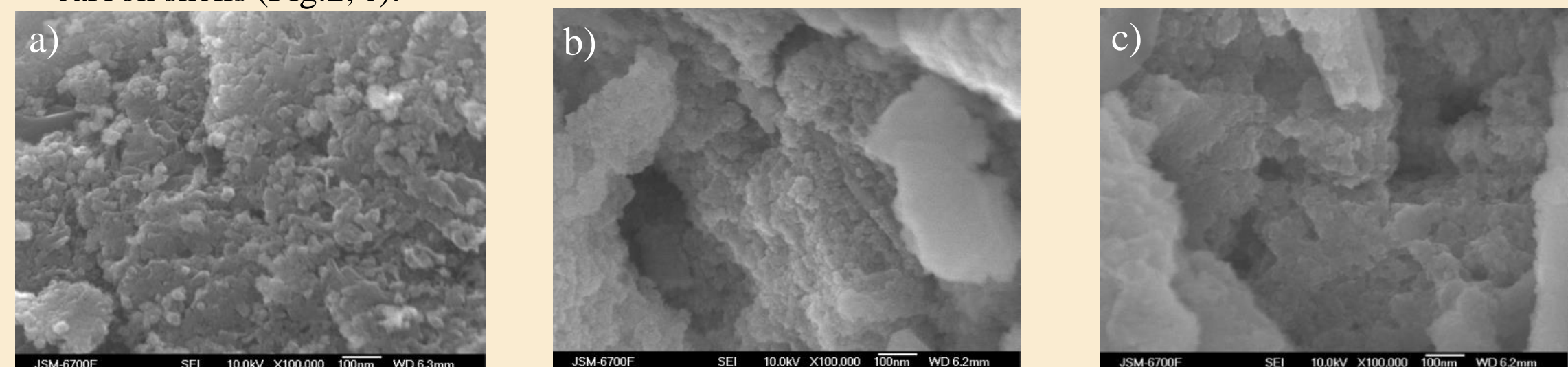
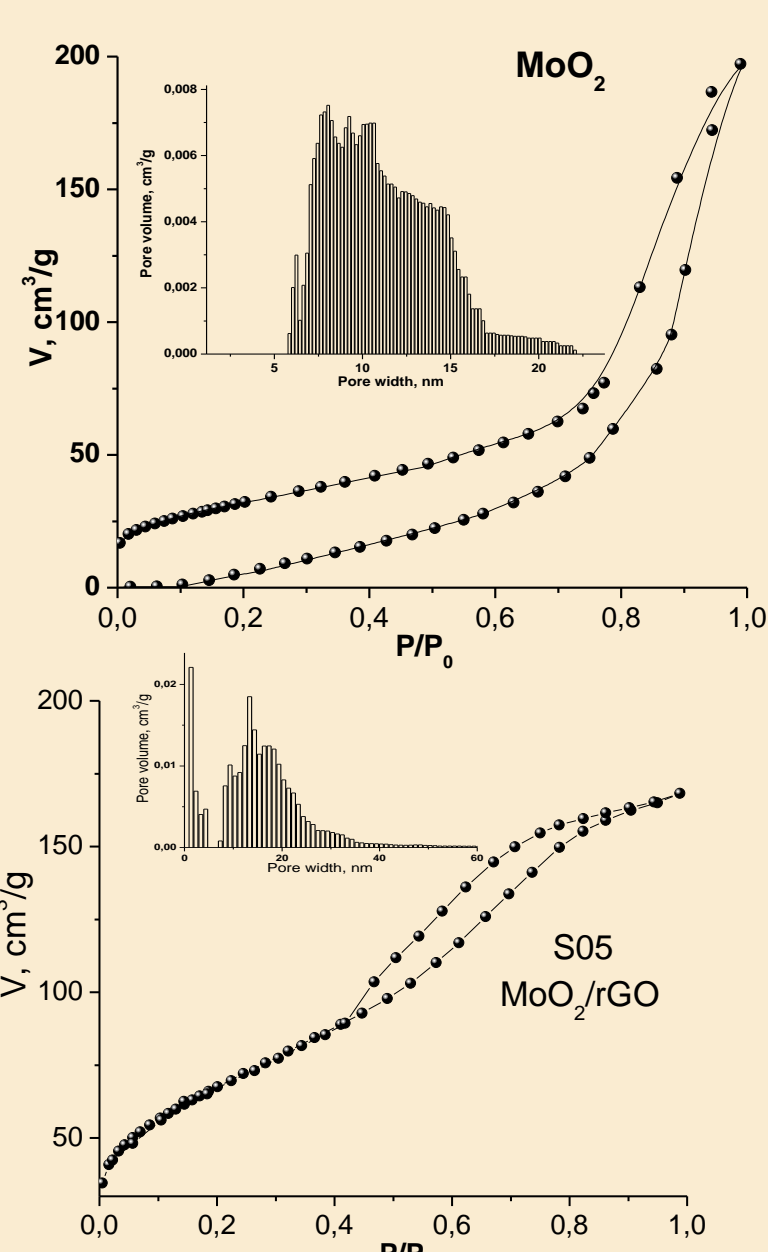


Fig.2. SEM images of samples S0(pure MoO₂), S05 and S10 (MoO₂/rGO composite materials).

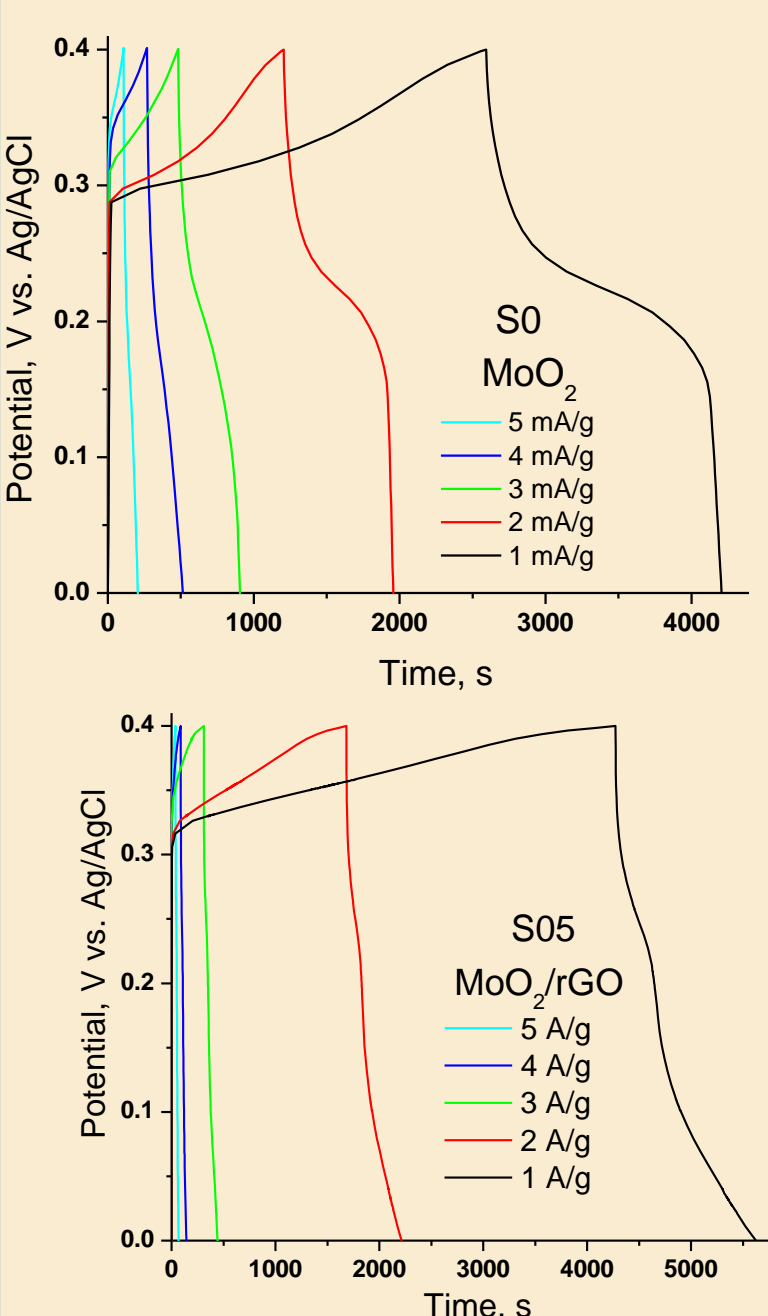
3 Low-temperature nitrogen porosimetry



The MoO₂ sample is characterized by a mesoporous structure only with a pore size in the range of 7-20 nm. The pore size distribution profile calculated for sample S05 is consistent with XRD data on the increase in the average particle size of MoO₂ component compared to pure MoO₂. The evolution isotherm and the PSD profile for sample S10 reflect the filling of small pores with rGO particles and/or the formation of pores with a smaller diameter due to the formation of the rGO microstructure.

Fig.3. Nitrogen adsorption-desorption isotherms (77 K) and PSD profiles for MoO₂ and MoO₂ / rGO

5 Charge-discharge cycling



Charge-discharge curves have been obtained in the potential window of 0-0.4 V at the galvanostatic conditions with a change in the current value in the range of 1 A g⁻¹-5 A g⁻¹. The maximum capacitance (395 F/g) has been obtained for sample S10. It should be noted that the specific capacitance of electrode based on the S05 sample is lower than that of pure MoO₂, which demonstrates the fundamental importance of optimizing both morphological and electrophysical properties.

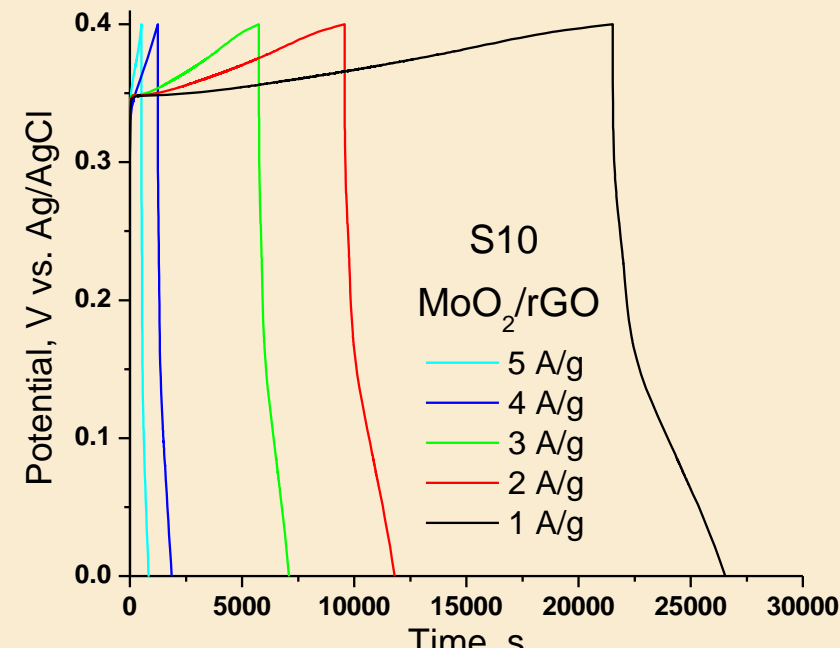


Fig.5. Charge-discharge curves of electrochemical capacitors based on MoO₂ and MoO₂/rGO

4 The electrical conductivity

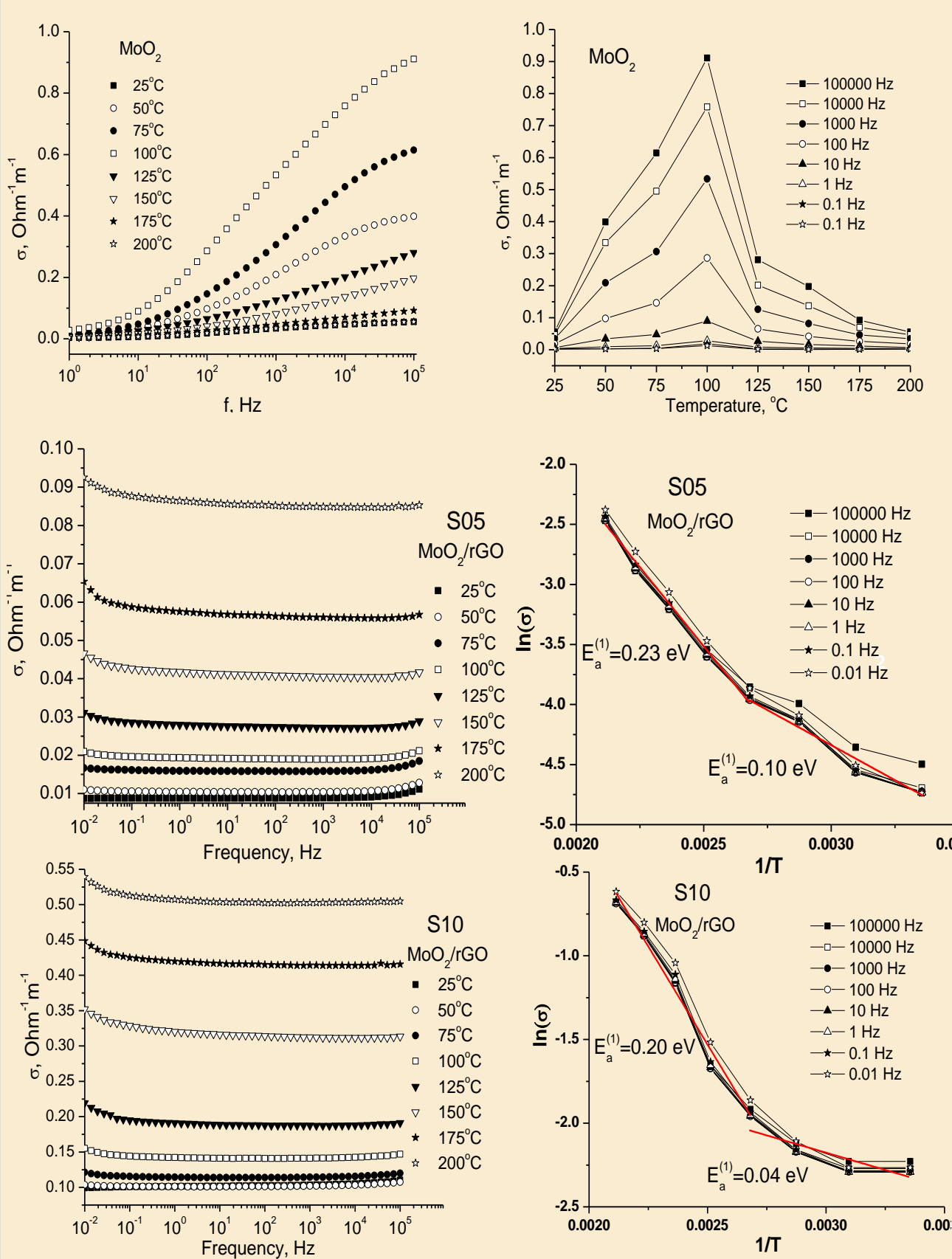


Fig. 4. (a, b) Electrical conductivity spectra, (e, f) Arrhenius plots of ac conductivities for MoO₂ /rGO composites (samples S05 and S10)

The electrical conductivity spectra $\sigma(f)$ of pure MoO₂, obtained at temperatures in the range of 25-200°C, increase with a change in frequency in the range of 10⁻²-10⁵ Hz (Fig.4, a). The conductivity spectra have been described by Johnson's law, which includes non-Debye mechanisms of charge carrier transport with phonon-controlled electron hopping between nanoparticles of the material. An increase in the conductivity can be explained by an increase in the efficiency of hopping proton conductivity. The linear behavior of the Arrhenius plot of the MoO₂ /rGO composites has been observed in two temperature ranges – R1 ($t < 100^\circ\text{C}$) and R2 ($t > 100^\circ\text{C}$). The activation energies for R1 are 0.10 and 0.04 eV for samples S05 and S10, respectively. An increase in temperature with a transition to R2 leads to an increase in activation energies to 0.23 and 0.20 eV for samples S05 and S10, respectively. It can be assumed that these two regions correspond to proton conductivity between physically intercalated water molecules (R1) and electron transfer between particles "MoO₂ core+rGO shell" (R2).

6 Electrochemical performance

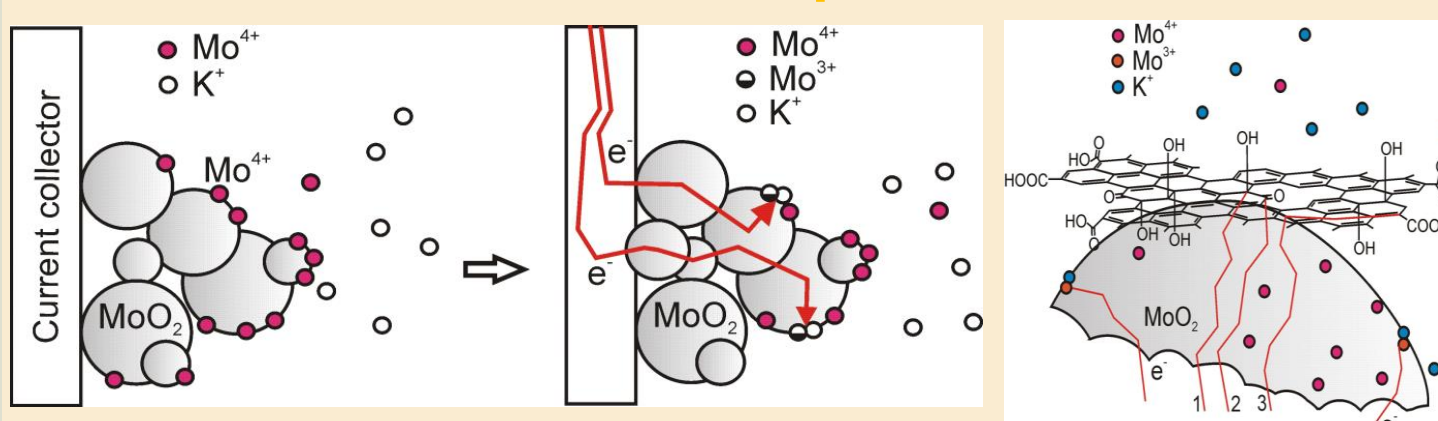


Fig. 6. (a) Scheme of possible mechanism of the reduction of Mo⁴⁺ on the surface of the MoO₂ electrode in an aqueous solution of KOH. (b) Possible mechanisms of the redox response of the MoO₂ /rGO electrode (numbers indicate the numbering of redox processes, including functional groups on the surface of graphene planes)

Local redistribution of electron density inside a nanoparticle leads to the process: Mo⁴⁺ + e⁻ ↔ Mo³⁺ with the formation of a surface complex (MoO₂)_{surface}+K⁺+e⁻=(MoOOK)_{surface}. The main contribution to the pseudocapacitive response of the composite electrode material is the result of redox processes Mo⁴⁺ ↔ Mo³⁺. Functional groups on the surface of rGO sheets also contribute to pseudocapacitance: -C-OH ↔ C=O + H⁺+e⁻ (1); C=O+e⁻ ↔ C-O (2); -COOH ↔ -COO+H⁺+e⁻ (3) (Fig.6 b). (Fig.7).

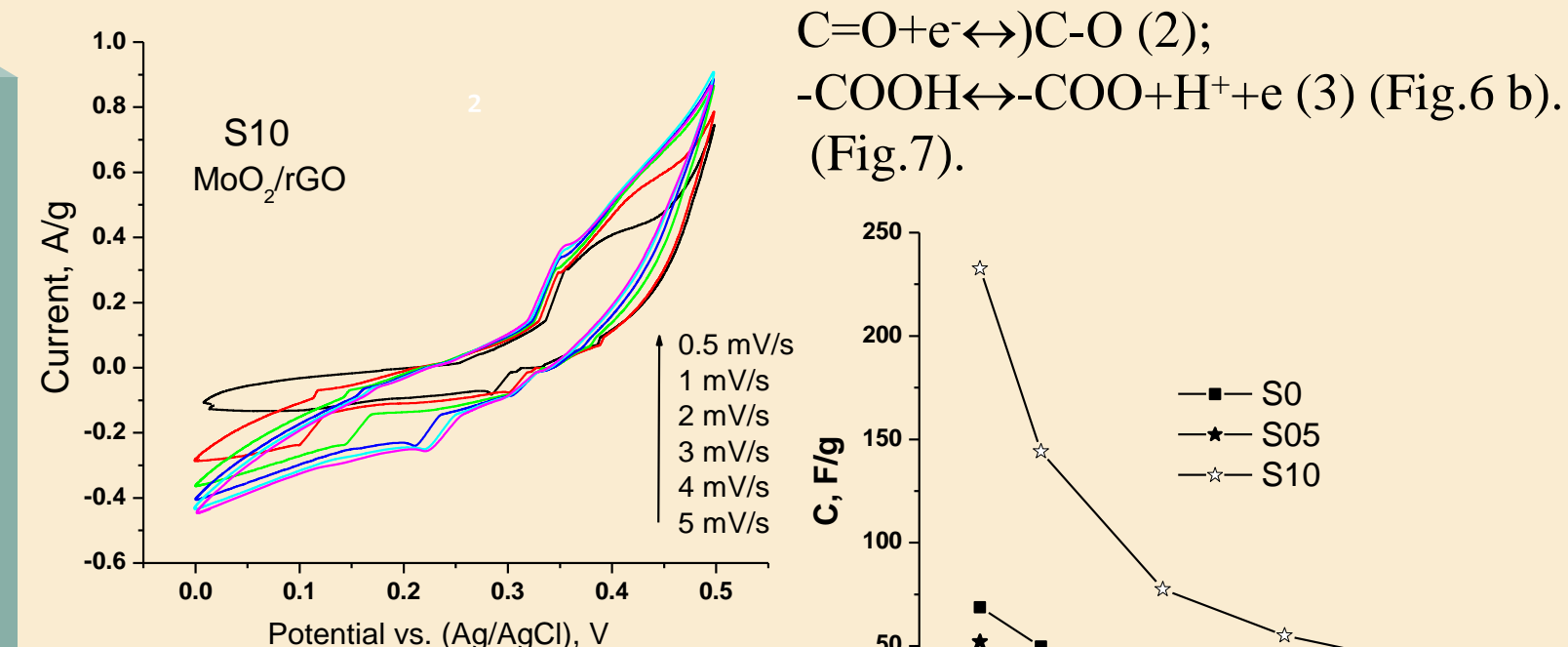


Fig.7. CVA curves obtained for an electrode based on MoO₂ / rGO materials (electrolyte - 1M KOH aqueous solution) (a)

Conclusions

Ultrafine MoO₂ as well as MoO₂/reduced graphene oxide (rGO) composites have been successfully prepared by common hydrothermal synthesis. The use of a graphene oxide (GO) colloidal solution, obtained by the modified Tour method as a component of the reaction mixture at a mass ratio of oxide and GO of 2:1, leads to an increase in the MoO₂ particle size. However, a twofold increase in the content of the graphene component leads to a decrease in the size of oxide particles and an increase in the specific surface area up to 421 m²/g with an increase in the content of both micro- and small mesopores. Interparticle electron hopping with an activation energy of about 0.34 eV is the dominant conductivity mechanism for ultrafine MoO₂. The presence of the rGO component leads to a decrease in the conductivity of the MoO₂ / rGO composite in the high frequency region compared to pure MoO₂; at frequencies less than 10 Hz, the values of the electrical conductivity of the composites are much higher. We can assume two mechanisms of MoO₂ / rGO electrical conductivity and electron transfer between particles "MoO₂ core+rGO shell". The specific capacitance of the MoO₂/rGO composite at a mass ratio of oxide and rGO of about 1:1, calculated on the basis of galvanostatic cycling data at 1 A/g, reaches 395 F/g. The capacitance of this material according to CVA data is 232 F/g. It can be assumed that a decrease in the size of MoO₂ particles with the optimization of ion and electron transport due to a balanced morphology makes it possible to obtain an electrode material with high electrochemical performance.