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Pseudocapacitance-based charge increase in MoS_2/C

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The electrochemical behavior of MoS_2/C composite in aqueous electrolytes was investigated using a three-electrode electrochemical cell. It was established that the studied system demonstrates the reversibility of redox processes, indicating the pseudocapacitance that makes this system functional. It was found that among the electrolytes used (KCl, RbCl, Li_2SO_4, Na_2SO_4, KOH), the aqueous KOH solution provides the largest contribution to the specific capacitance of the electrochemical device. The manifestations of pseudocapacitance (depending on the accumulated charge and the potential value) were analyzed from a thermodynamic point of view.

Keywords: EDL, PCM, molybdenum disulfide composite, pseudocapacitance, redox process, three-electrode electrochemical cell.

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Introduction

Synthesis and modification methods refinement for the porous carbon materials has almost reached rather particular limit: specific capacitance growth of the charge storage devices after such methods application does not exceed ~1.5%. That's why new capacitance improvement approaches are required.

Some electrochemically active materials that provide pseudocapacitance (much larger than EDL's capacitance) can be used to increase the EC capacitance.

To increase the capacity of the EC, some electrochemically active substances are chosen as electrodes, providing a pseudocapacitance (much higher than the capacity of the EDL. Pseudocapacitive charge accumulation is significantly different from the electrostatic mechanism that determines the capacity of the EDL. For pseudocapacitance, Faradaic charge transfer in the electrode porous layer occurs through a thermodynamically and kinetically favorable electrochemical reduction-oxidation reaction [1]. This redox reaction largely depends on the electrode potential, since the change in the charge amount dq that occurs as a result of this reaction is associated with a change in the electrode potential dU. The $\underline{dq/dU}$ dependence is called the pseudocapacitance created by the redox reaction, analogous to the similar electrochemical reaction in batteries. The redox reaction in the electrode layer must be electrochemically reversible or partially reversible to ensure an efficient charge/discharge process. If the near-surface layer of the EC electrode consists entirely of a reversible electrochemically active material, the electrode will behave like a battery. However, in a pseudocapacitive electrode layer containing both an electrochemically inert material (e.g., activated carbon) and an electrochemically active substance (e.g., a redox material), the charge and discharge will involve two processes: 1) charge/discharge of the EDL; 2) an electrochemical redox process (redox reaction).

I. Experimental, discussion of the results

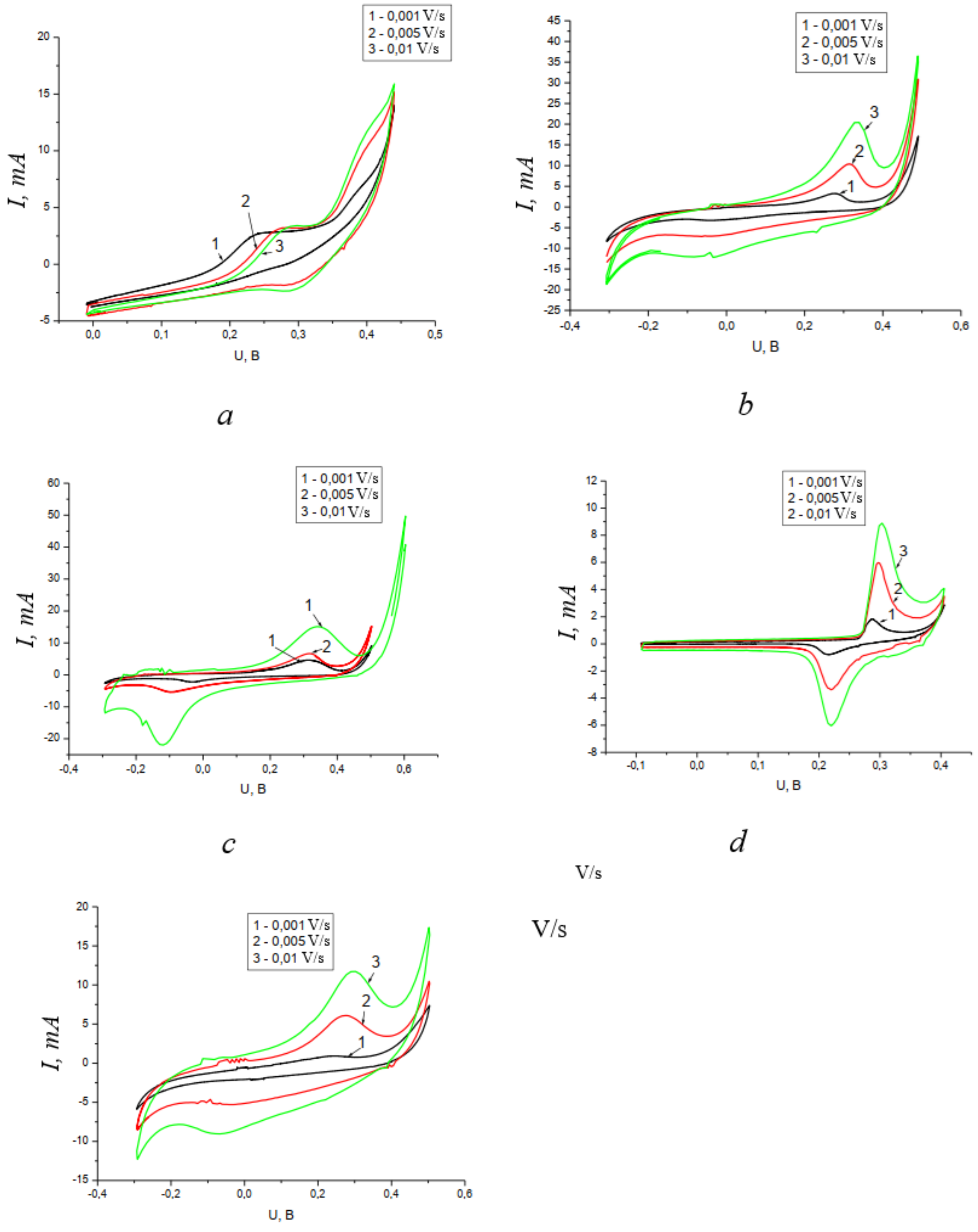
Molybdenum disulfide and MoS_2/C composites in aqueous electrolytes were used to study electrochemical behavior. For this purpose, three-electrode electrochemical cells were used, where the materials under study were the working electrodes, the platinum electrode was the auxiliary electrode, and the Ag/AgCl chlorine-silver electrode was the reference electrode. Aqueous solutions of optimal concentrations (with the highest specific conductivity) of KOH, KCl, RbCl, Li_2SO_4 and Na_2SO_4 were used as electrolytes. Electrochemical studies were carried out using an Autolab PGSTAT/FRA-2 spectrometer by galvanostatic and potentiodynamic methods.

As can be seen from Fig. 1, all the electrochemical systems under study (to one degree or another) demonstrate reversible redox peaks that indicates the pseudocapacitive properties of molybdenum disulfide.

In general, two possible charge storage mechanisms can be considered for molybdenum disulfide. The first and dominant one is based on pseudocapacitive behavior due to the Faradaic charge transfer process [2]. During fast reversible redox reactions ions like hydrogen protons or Li^+, K^+, Na^+, Rb^+ cations can diffuse between the layers of the MoS_2 structure:

$$MoS_2 + (H^+, Li^+, Na^+, K^+, Rb^+) + e^- \leftrightarrow MoS - S(H^+, Li^+, Na^+, K^+, Rb^+).$$

Among them, the Li^+ ion is characterized by the smallest radius (Table 1), followed by an increase in the



a

b

c

d

V/s

V/s

e

Fig. 1. Cyclic voltammograms of MoS_2 in different electrolytes : *a* - KOH; *b* - KCl; *c* - RbCl; *d* - Li_2SO_4; *e* - Na_2SO_4

size of the ions, and the largest among them is the Rb^+ ion. At first glance, the relatively large rubidium ion should pass between water molecules in the electrolyte much more slowly than the lithium ion. However, as we can see in Table 1, the lithium cation mobility is minimal. And the fact that ions in the solution are surrounded by solvent molecules can explain such mobility. Despite the fact that all these cations have the same charge +1, the field strengths created by these cations differ significantly: the smaller ion size, the higher field strength it creates. That is why the smallest of the cations: the lithium ion, is actually the largest, since it is surrounded by a large number of water molecular layers. The number of water molecules surrounding the sodium cation is somewhat smaller, and accordingly its sizes in aqueous solutions are smaller. The molecular "shell" of the potassium cation is even thinner, and the smallest size in aqueous solutions belongs to the largest rubidium cation.

Table 1.

Some characteristics of hydrogen ions and alkali metals

Ion radius, nm				
H^+	Li^+	Na^+	K^+	Rb^+
0.054	0.068	0.098	0.133	0.149
Ion mobility (in relative units)				
350	38.6	50.1	73.5	77.8

An interesting fact is that the hydrogen cation (Table 1) has a very high mobility, which is caused by a different mechanism of movement. It is known that there are no H^+ ions in water, but H_3O^+ (and these ions in turn can combine with water molecules, forming $H_5O_2^+$, $H_7O_3^+$, $H_9O_4^+$). It is not the H_3O^+ ion itself that moves, but the proton jumps from one water molecule to another, transferring a positive charge according to the scheme (Fig. 2).

Fig. 2. Hydrogen proton movement scheme.

Also the same movement is correct for the OH^- (fig. 3).

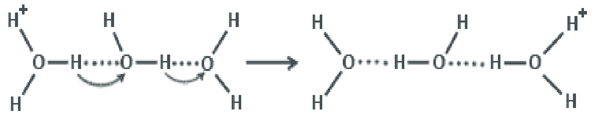


Fig. 3. OH^- movement scheme.

Thus, it can be assumed that the contribution of fast reversible redox reactions of ions to the specific capacity of the electrochemical devices under study can be quite large when using an aqueous KOH solution electrolyte.

Another non-Faradaic process is associated with the double electric layer formation at the electrode/electrolyte interface during the protons or cations adsorption on the MoS_2 surface:

$$MoS_2\ surface + (H^+, Li^+, Na^+, K^+, Rb^+) + e^- \leftrightarrow MoS_2(H^+, Li^+, Na^+, K^+, Rb^+)\ surface$$

According to the CVA results (cyclic voltammogram) data, it was found that the discharge specific capacitance value (Table 2) is the largest (85.1 F/g) when using a 33% aqueous KOH solution as an electrolyte, probably due to the easy access of K^+ ions to the molybdenum disulfide inner layers, in comparison with other ions.

Table 2.

Specific capacitance for MoS_2 in different electrolytes, calculated by CVA

Scan speed., V/s	KOH		KCl		RbCl	
	C_{charge} F/g	$C_{discharge}$ F/g	C_{charge} F/g	$C_{discharge}$ F/g	C_{charge}, F/g	$C_{discharge}$ F/g
0.001	91.3	85.1	71.4	60.3	88.4	83.0
0.005	65.2	59.3	40.8	39.8	57.8	56.1
0.01	39.7	36.4	35.6	33.6	35.9	35.8
	Li_2SO_4			Na_2SO_4		
0.001	69.8		66.5	66.2	55.2	
0.005	39.8		35.9	30.2	28.7	
0.01	29.9		25.6	25.2	24.9	

As can be seen from Fig. 1a, the difference between the anodic and cathodic peaks is 0.013–0.037 V (depending on the scan rate) which indicates that Faradaic processes are reversible. the Rendles-Shevchyk equation can be written for quasi-reversible systems, that defines the diffusion coefficient D at 298 K as the slope of the linear plot of the dependence of the peak currents I_p on the square root of the scan rate s:

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} c^0 s^{1/2} \qquad (1)$$

where n – quantity of electrons that take part in the reaction, A – surface area, c^0 – initial concentration of reagents.

Thus, the ion diffusion coefficient calculated according to (1) for pure molybdenum disulfide (KOH electrolyte) is $3.62 \cdot 10^{-13}$ cm²/s. And the straight line characterizing the dependence of the peak current value on the scan rate square root (Fig. 4) does not cross the origin. It indicates complex processes of a certain limited speed that occur during the charge/discharge process.

The study of the electrochemical properties of the MoS_2/C composite was carried out using aqueous KOH solution as electrolyte. When the composite contains 90% molybdenum disulfide, cyclic voltammograms (Fig. 5a) taken at different scan rates in the potential range of 0.1–

0.45 V clearly show redox peaks, and the form of the anodic peak is complex with maxima at 0.32 and 0.38 V. This indicates that the contribution to the composites' conductivity is made by both the capacitive nature of charge accumulation inherent in highly conductive carbon (which improves charge transfer during charge/discharge processes) and the fast reversible Faradaic processes inherent in molybdenum disulfide.

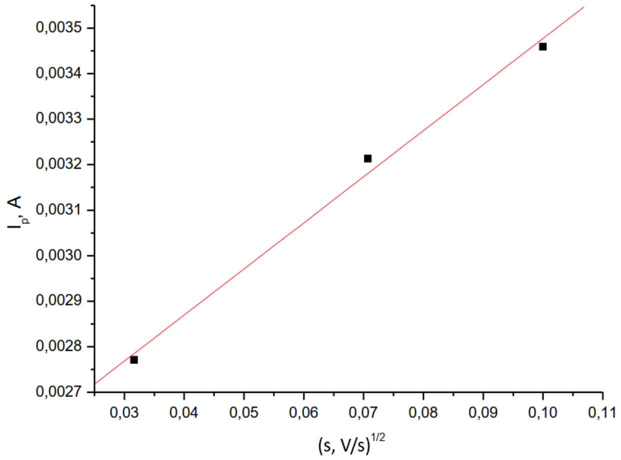


Fig. 4. Magnitude dependence of the current peaks on the square root of the scan rate (S), calculated from the CVA for MoS_2 in aqueous KOH solution.

Since carbon, as a porous structure, is characterized by a large specific surface area, it can effectively reduce ion diffusion path, contributing to the rapid electronic charge transfer between the electrode and the electrolyte that leads to an increase in the specific characteristics of the studied materials. But with carbon content 80% increase in the composite the cyclic voltammograms' shape starts resembling the rectangular one inherent in carbon, and the value of the specific capacitance (Table 3) decreases. It is probably due to the absence of fast reversible Faradaic processes, since the amount of molybdenum disulfide decreases.

Table 3.

The values of the specific capacitances of MoS_2/C composites at a scan rate of 0.001 V/s

Material	C_{charge}, F/g	$C_{discharge}$, F/g
MoS_2	91.3	85.1
MoS_2/C=90/10	101.1	90.5
MoS_2/C=50/50	112.9	92.6
MoS_2/C=30/70	137.4	107.6
MoS_2/C=20/80	106.6	94.8
MoS_2/C=10/90	93.9	82.0

As can be seen from Table 3, the MoS_2/C composite with a carbon content of 70% has the highest specific capacitance, that is associated with the best combination of the two charge accumulation mechanisms described above, which, as can be seen from Fig. 5, most likely make

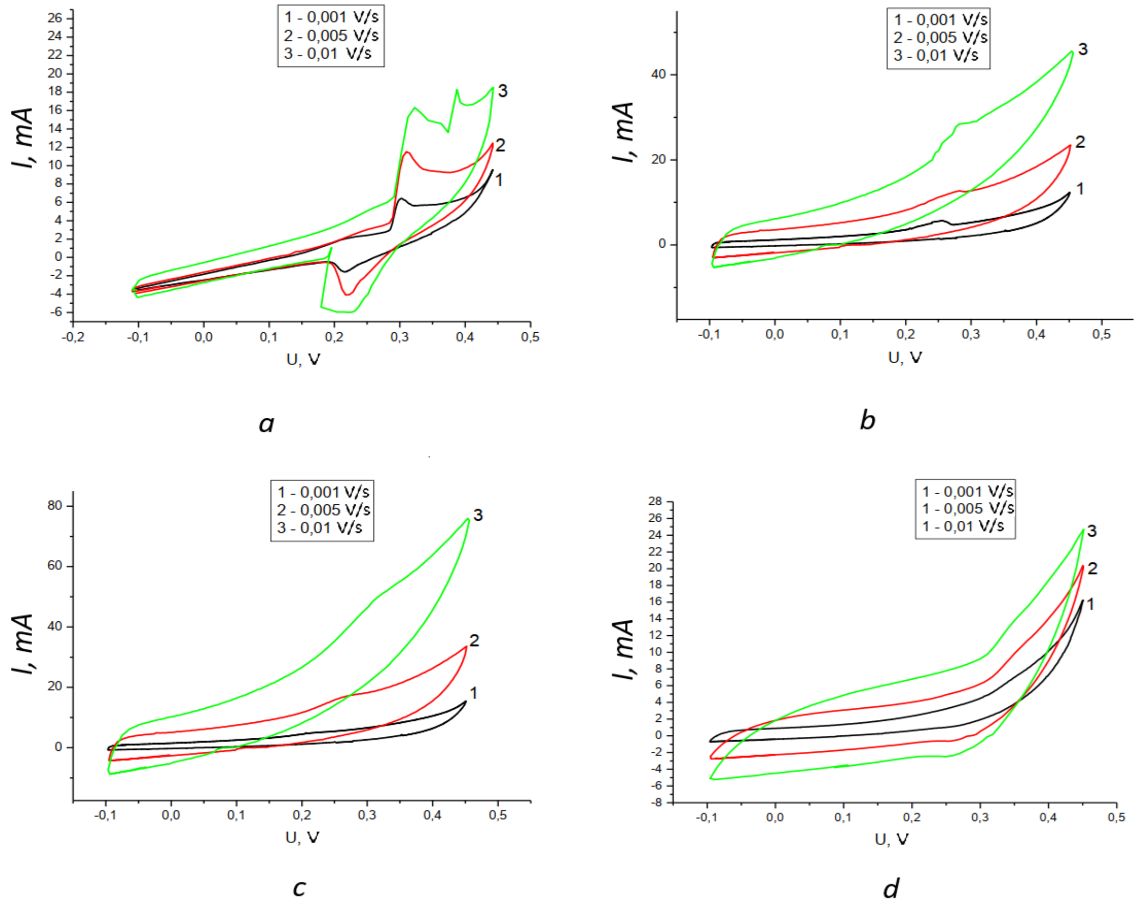


Fig. 5. Cyclic voltammograms of MoS_2/C composites with different PCM contents:
a – 10%, *b* – 50%, *c* – 70%, *d* – 80%.

a proportional contribution to the increase in the specific capacitance. This assumption is confirmed by the authors of [3], where it was experimentally proven that the MoS_2/C composite in the ratio of the initial components 1:2 demonstrates the best electrochemical characteristics as an anode material in lithium current sources, due to Faradaic and capacitive charge accumulation. From a thermodynamic point of view, pseudocapacitance arises whenever some quantity y is proportional to the passed charge and depends on the potential, then the following equation can be written:

$$\frac{y}{1-y} = Kexp\left(\frac{UF}{RT}\right) \tag{2}$$

The quantity y can be the solid angle θ of the electrode surface, which is necessary for the deposition of adatoms, the value of the partial absorption X at some intercalations of the host material, or some value of the transition of the oxidant to the reductant (or vice versa) in redox systems. Each of the above examples is formally described by the general method of the electrode transfer process between the oxidant Ox and the reductant Red, as follows:

$$Ox + ze \leftrightarrow Red \tag{3}$$

Differentiating equation (2) with respect to dU, we obtain:

$$\frac{dy}{dU} = \frac{F}{RT} \cdot \frac{Kexp(UF/RT)}{[1+Kexp(UF/RT)]^2} \tag{4}$$

and since y is a quantity proportional to the charge passed in each process, dy/dU is a quantity proportional to the corresponding capacitance. The maximum pseudocapacitance occurs at half the redox pair conversion or at half the surface (or volume) of the host material ($\theta = 1/2$ or $X = 1/2$) and can be more than 2000 $\mu F \cdot cm^{-2}$. Thus, the capacitance values in pseudocapacitive systems can significantly exceed (10–100 times) the capacitance values of the EDL [4].

Equation (4) describes the behavior of a pseudocapacitive capacitor system for non-interacting parts ($g = 0$). However, when interactions occur between its parts in the system ($g \neq 0$), it is necessary to include an additional interaction term (e.g., $e^{\pm gy}$) in the right-hand side of equation (4). Then the capacitance dy/dU will take on smaller values, but will be in a larger voltage range. There are two explanations for the nature of pseudocapacitance: the first explains it from the point of view of equilibrium thermodynamic processes; the second is based on a kinetic approach to Faradaic processes under the condition of deviation from the equilibrium state. In real systems, various interactions associated with pseudocapacitance can occur. Thus, chemisorption usually occurs in polar bonds of the adsorbate with the electrode, which experience repulsion between their electronic orbitals. A change in the surface distribution of electrons can also be observed – “forced (induced) by inhomogeneity”. To take these effects into account it is sufficient to introduce an additional energy term $g\theta$ into the isotherm that has the same configuration term Gibbs energy $RTln\theta/(1-\theta)$. Then the electrosorption isotherm will take the form:

$$\frac{\theta}{1-\theta} = Kexp(-g\theta) \cdot c_{H^+} exp(UF/RT) \tag{5}$$

Here $Kexp(-g\theta)$ is the equilibrium constant of the adsorption-dependent zone, which differs from the constant K by the Langmuir exponential coefficient $-g\theta$. Thus, K decreases with increasing θ for positive values of g that corresponds to pairwise repulsions of the adsorbate in the adsorption layer. To determine the pseudocapacitance C_φ, we use the relationship:

$$C_\varphi = \frac{q_1F}{RT} \cdot \frac{\theta(1-\theta)}{1+g\theta(1+\theta)} \tag{6}$$

The maximum value of pseudocapacitance in this case is smaller than the maximum of pseudocapacitance of the Langmuir-type electrochemical isotherm at $\theta = 0.5$. In addition, the values of C_φ are in a wider range of potentials (Fig. 6).

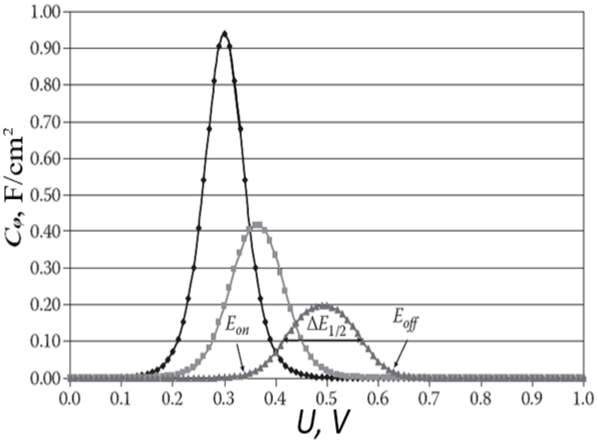


Fig. 6. The dependence of C_φ on the electrode potential was calculated for three values
(*a*) $g = 0$ –♦–; (*b*) $g = 5$ –■–; (*c*) $g = 15$ –▲–

It is worth noting that the interaction coefficient increase for values of $g > 0$ leads to a more complex electrosorption process, since the part of the occupied surface θ increases with increasing potential. So it is necessary to apply a large potential to achieve a given value of θ. The opposite effect occurs for $-4 \leq g \leq 0$. To achieve full occupancy $\theta \rightarrow 1$ a smaller effective range of potentials is required than for $g > 0$. By taking the formula (6) logarithmically, we obtain:

$$ln\frac{\theta}{1-\theta} + g\theta = lnKc_{H^+} + \frac{UF}{RT} \tag{7}$$

By differentiating with respect to U, we obtain two mutually inverse components of the capacitance: $RT/q_1F \cdot dln(\theta/1-\theta)$, which corresponds to the inverse of the Langmuir-type capacitance and $(RT/q_1F) \cdot g$ – the inverse of the Temkin-type capacitance, which arises due to surface inhomogeneity. For intermediate values of θ ($0.3 < \theta < 0.7$) and large values of g ($g > 10$), θ depends linearly on U, i.e., the pseudocapacitance C_φ almost does not change with a change in potential. Let us consider the kinetic explanation of the pseudocapacitance. For this, the Faraday current *i* is written in the form of the Butler-Volmer equation:

$$\frac{i}{zF} = k_1 c_{H^+}(1-\theta)exp\left(\beta\frac{UF}{RT}\right) - k_{-1}\theta exp - \left((1-\beta)\frac{UF}{RT}\right) \tag{8}$$

where k_1 and k_{-1} are constants for the forward and reverse directions of process *I*, for which $z = 1$ and β is the barrier symmetry factor for the charge transfer process (β = 0.5). At equilibrium i = 0, the function $\theta(U)$ can be written as

$$\theta = \frac{K_1 c_{H^+} exp(UF/RT)}{1 + K_1 c_{H^+} exp(UF/RT)} \tag{9}$$

From the dependence $\theta(U)$ we can obtain $d\theta/dt$ as:

$$d\theta/dt = \frac{K_1 c_{H^+}}{K_1 c_{H^+} + exp - [U(t)F/RT]} \cdot \frac{F}{RT} \cdot exp[U(t)F/RT] \cdot s \tag{10}$$

where s is the linear change in potential, which is determined by $U(t) = U(t = 0) + st$. Then the Faradaic current density ($q1 \cdot d\theta/dt$) for a one-electron process $z = 1$ will be determined by the formula:

$$i/F = \frac{K_1 c_{H^+} [U(t)F/RT]}{\{K_1 c_{H^+} + \exp - [U(t)F/RT]\}^2} \cdot s \tag{11}$$

For 0.05 < θ < 0.95 the current for the charge-discharge of the pseudocapacitance is greater than for the capacitance of the electric double layer. Under fully reversible conditions, the maximum pseudocapacitance is achieved and the electrochemical processes occurring on the electrode surfaces remain in equilibrium and do not depend on the (sign) potential. In an electrochemical system where the accumulation of charge occurs due to redox reactions, the Nernst equation will look like:

$$E = E^0 + (F/RT)ln[Ox]/[Red] \tag{12}$$

where *[Ox]* and *[Red]* are the concentration or activity of the reactants. The above equation can be written in terms of the molar quantity Q of the redox substances ($Q \equiv$ *total [Ox] + [Red]*):

$$E = E^0 + (F/RT)ln[Ox/Q]/[Red/Q]$$

or

$$E = E^0 + (RT/F)ln[Ox/Q]/(1 - [Ox/Q])$$

whence *[Ox] + [Red] = Q* (in a given volume). The last equation can be rewritten as follows:

$$[Ox/Q]/(1 - [Ox/Q]) = exp(E - E_0)F/RT = exp(\Delta E \cdot F/RT)$$

where E^0 is the normal potential of the redox pair. Differentiating by ΔE we find the nominal value of the capacitance that can be determined experimentally:

$$\frac{C}{Q} = d[Ox/Q]dE = \frac{F/RT \cdot exp(\Delta E \cdot F/RT)}{[1 + exp(\Delta E \cdot F/RT)]^2} \tag{13}$$

The capacitance in equation (13) is considered a pseudocapacitance because it appears as a reversible Faradaic reaction result in one direction or another. Equation (13) is “universal” for this type of system; the right-hand side takes on a maximum of 10 Q when *Ox/Q = Red/Q* = 0.5. For a 5 M solution of a one-electron redox reagent ($5 \cdot 10^{-3}$ mol·cm^{-3}), the value of Q is $5 \cdot 10^{-3}$ F·cm^{-3} or approximately 500 C·cm^{-3}. Then the pseudocapacitance (*[Ox] = [Red]*) maximum value is 5000 F·cm^{-3}. It is worth noticing that the specific pseudocapacitance of redox reactions is much larger than the specific capacitance of the EDL. Fig. 7 shows the calculated total capacitance as a function of electrode potential.

But for redox pseudocapacitances based on strong solutions of redox pairs, the effective working potential range (as follows from the formula) is only approximately ±100 mV of the pseudocapacitance maximum potential. In addition, diffusion strongly affects the reversibility of such a system.

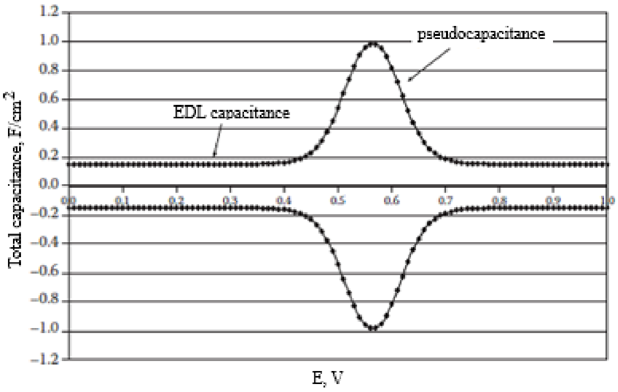


Fig. 7. Total capacitance calculated as an electrode potential function.

However, when several redox pairs are incorporated into the surface structure (as in the case of RuO$_2$) a much larger working potential range can be achieved: up to 1.4 V. Another pseudocapacitance type is based on intercalation processes, that have thermodynamic equation of sorption described by the following equation:

$$E = E^0 + (RT/F)ln[X/1 - X] \qquad (14)$$

where X is the three-dimensional position of partial filling by sorbed impurities of atoms or ions (for example Li^+ ions). (14) shows that Li-ion intercalation batteries can be considered pseudocapacitors of some kind. The magnitude of the charge constantly relies on the potential, but for system like this the capacitance response time is greater than capacitors with EDL have, due to interlayer diffusion in the host lattice.

Another source of pseudocapacitance is the so-called "specific adsorption" of ions (usually anions) on the electrodes. It appears as a result of the "specific" electronic interaction between the valence electrons of the ions and the electrodes' surface orbitals and is accompanied by partial charge transfer. The quasi-chemical equation for A^- anions specific adsorption on the electrode M can be written in the following form:

$$M + A^- \rightarrow M/A^{(1-\delta)} + \delta e$$

where δ is some part of the electron charge. This process has the acid-base nature of the Lewis donor-acceptor interaction; the anion is the donor. Adsorption occurs more strongly for a positively charged electrode, but at zero potential of many anions. The value of δ (or $1 - \delta$) is a component of the so-called "electrosorption valence" of the anion, that describes its chemisorption behavior on the electrode. It should be noted that pseudocapacitance value caused by the specific adsorption is insignificant. But it can emerge in electrochemical systems along with other capacitance main components.

Conclusions

1. It is shown that there are two mechanisms of molybdenum accumulation in electrochemical systems. The predominant one is Faradaic charge transfer due to fast reversible redox reactions when hydrogen protons and Li^+, K^+, Na^+ or Rb^+ cations diffuse between the layers of the MoS_2 structure.
2. The electrochemical behavior of the MoS_2/C composition with a 90% molybdenum disulfide content indicates that in the potential zones of 0.1–0.45 V there are clearly exhibited redox peaks with maxima at 0.32 and 0.38 V, i.e. the contribution to the composite conductivity is provided both by capacitive charge accumulation and by fast reversible Faradaic processes.
3. The pseudocapacitance exhibition is analyzed from a thermodynamic point of view, when the magnitude of the oxidant transition into the reductant or vice versa in redox systems is proportional to the transferred charge and accordingly depends on the potential $\frac{y}{1-y} = Kexp\left(\frac{UF}{RT}\right)$, where K is the equilibrium constant, F is the Faraday number, R is the gas constant, and T is the absolute temperature.

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Псевдоємнісне накопичення заряду в MoS_2/C

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Досліджена електрохімічна поведінка дисульфіду титану та композиту MoS_2/C у водних електролітах із використанням трьохелектродної електрохімічної комірки. Встановлено, що досліджувана система демонструє наявність оборотності окислювально-відновних процесів, що свідчить про псевдоємнісний характер функціонування даної системи. Виявлено, що посеред використаних електролітів (KCl, RbCl, Li_2SO_4, Na_2SO_4, KOH) найбільший вклад у величину питомої ємності електрохімічного пристрою вносить водний розчин KOH. Проаналізовано з термодинамічної точки зору прояви псевдоємності залежно від накопиченого заряду і величини потенціалу.

Ключові слова: ПЕШ, НВМ, дисульфід молібдену, композит, псевдоємність, окислювально-відновна реакція, трьохелектродна електрохімічна комірка.