Thin-film technologies for producing electrode materials for chemical sources of current (CSC) and ultra-high-volume capacitor structures (UCS)

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Abstract. This paper describes analysis of thin-film technologies for promising CSC and UCS. It was shown that the stored energy amount is determined by the work to move charges in the preset direction. This relationship defines the CSC and UCS energy intensity and shows that the process of electric energy storage in them is the same and mainly determined by the polarization effects in the system.

1. Introduction
Electronics, instrumentation, power generation, transportation, medicine and numerous other areas of science and technology suggest a steady off-line supply sources share increase. Today, the best batteries samples are the secondary chemical sources of current (CSC) that provide energy intensities of around 250 W h/kg, and intensive research is under way to develop over the next 5 years energy storage units with the storage capacity of up to 450 to 500 W h/kg, and in the long term - up to the theoretically justified limit of 1000 to 1200 W h/kg. Energy intensity of ultra-high-volume capacitor structures (UCS) is 10 to 20 W h/kg, intensive research is under way to attain specific energy intensity of 20 to 40 W h/kg and 220 to 250 W h/kg for the hybrid UCS. Conventional CSC and electrolytic UCS design is targeted at thick-film electrode materials formation, where chemically active CSC substance and ultra-porous UCS material are applied in paste form in a thick (30–60 µm) layer on aluminum or copper foil. This fairly cheap and productive technology is the most widely used for industrial purposes. However, recently, there developed a trend to reduce energy intensity of CSC produced by this technology [1–2]. In this way, there is a need to seek and develop new technologies that will provide required CSC and UCS energy intensity growth. The most perspective from this point of view are the thin-film technologies that have recently begun to develop which became actively developing lately [3–5].

2. Theoretical study of CSC and electrolytic UCS electrode materials thin-film formation technologies
The energy can be supplied to and extracted from the system in the form of heat or work [6–7]:

\[ E = T \cdot S \pm \sum_{i=0}^{n} A_i \]

where \( E \) is the energy supplied to the system; \( T \) is the system temperature; \( S \) is the system entropy; \( A_i \) is the work performed by the system (when energy is extracted) or +\( A_i \), when energy is supplied to the system. For the real, irreversible processes the work, which can be supplied to the system or extracted
from it, is written as the Product of two values - extensive (x) and intensive (y) ones. In this case, equation (1) should be written as follows:

$$dE = d(T \cdot S) + d(P \cdot V) + (\delta \cdot F) + d(\varphi \cdot q) + d\sum(\mu \cdot n_i)$$

(2)

where $T$ – is the temperature; $P$ – is the pressure; $\delta$ – is the surface energy; $\varphi$ – is the electric potential; $\mu_i$ – is the chemical potential - extensive parameters; $S$ – is the entropy; $V$ – is the volume; $q$ – is the charge; $n_i$ – is the molar quantity - intensive parameters.

With the structural elements reduction to the nanodimensional values extensive parameters begin to depend on intensive ones. In this case, the energy intensity of nanostructured systems is much higher than the energy intensity of monolithics, and numerous experiments have unambiguously confirmed that fact [8–9]. By [10] shown that the thermodynamic and electrostatic accounting of polarization interactions of particles in the system lead to the same result - chemical potential of the molecule surrounded by its neighbors, producing an effective field $E$, is equal to the polarization work of the molecule under discussion. In this case, the chemical potential of the molecule (to an accuracy of up to the additive constant KT independent of the electric-field strength) can be represented as:

$$\mu = -PE = A_i$$

(3)

where $P$ – is the dipole moment; $E$ – is the electrical field strength; $A_i$ – is the electric field work. Formula (3) as a result of a simple conversion can be written as:

$$dA_i = -ed\varphi$$

(4)

In this case, the Gibbs potential under the isobarometric conditions can be written as [10]:

$$dG_{pv} = \sum N_i d\mu_i = \sum N_i ed\varphi = \sum N_i E dp_i$$

(5)

Taking into account the electrocapillarity effects that occur during the two contiguous phases interfaces formation, the Gibbs potential is written as follows:

$$dG_s = \delta dF + Edp$$

(6)

where $E$ – is the electrical field strength; $P$ – is the dipole moment; $\delta$ – is the surface tension; $F$ – is the surface area.

Using the Maxwell rearrangement and the Poisson’s equation for equation (6), we obtain the fundamental electrocapillary equation [10–13]:

$$\frac{\partial \delta}{\partial x} = -\rho^\text{free} + \rho^\text{bound} = -q$$

(7)

where $\rho^\text{free}$ and $\rho^\text{bound}$ – are the free and bound charges surface density; $\partial x$ – is the interface barrier jump. Based on equations (3, 4 and 7) [10, 13] molecule polarization work can be determined $A_i$.

$$A_i = pE = \mu$$

(8)

Equation (8) allows to draw the conclusion that the chemical potential of the molecule surrounded by its neighbors, producing an effective field $E$, is equal to the polarization work of this molecule. Differential equation (8) can be written as

$$dA_i = pdE + Edp = d\mu$$

(9)

In accordance with the equation of the first and second laws of Thermodynamics it can be written as [6, 10]

$$dG_{(\delta T=0, dp=0)} = \sum N_i d\mu_i = N_i ed\Delta \varphi$$

(10)

Ratio (10) is widely used in the theory of electrochemical cells that, first of all, convert the energy of a chemical reaction into electrical energy [10, 13]. The integrated form of equation can be written as follows:

$$\Delta G^*_{ch} = \sum \Delta G^*_{con} - G^*_{finit} = \sum N_i \mu^*_{con} - \sum N_i \mu^*_{init} = z e \Delta \varphi$$

(11)

where $z = \sum N_i e$ – is the amount of electricity (charge) that has passed through the external electrochemical cell circuit. This charge, as follows from the equation (11), is proportional to the amount of the cell substance that reacted, $EMF = \sum \Delta \varphi_i$ is the cell electromotive force (EMF) equal to the sum of the barrier jumps $\sum \Delta \varphi_i$. In this case, the cell EMF on a first approximation can be estimated as:
EMF = \frac{\Delta G_{\text{react}}}{z} \quad (12)

Equations (11), (12) suggests that thin film structures less heat loss. This is due to the fact that in thin layers significantly less electrical resistance and, accordingly, reduced heat generation during the electron passes through them.

3. System without chemical reactions (big capacity capacitors electrolytic structures)

The major parameter of the systems accumulating electrical energy without chemical reactions is the electric capacitance. Differential capacity value can be found using electrocapillary curves [10, 13]

\[- \frac{d^2\delta}{d\phi^2} = \frac{dq}{d\varphi} = C_d \quad (13)\]

By [10, 13, 14] was shown the influence of bound and free charges on the capacitance of DEL that were called dipole and electronic component respectively. Lippmann equation in this case can be converted to mean:

\[\frac{d\varphi}{d\rho} = \frac{d\varphi_e}{d\rho} + \frac{d\varphi_d}{d\rho} \quad \text{or} \quad C^{-1} = C_e^{-1} + C_d^{-1} \quad (14)\]

where \(C_e^{-1}\) – is the electronic part of the DEL capacitance; \(C_d^{-1}\) – is the dipole part of the DEL capacitance.

Expression for the DEL electronic part capacitance can be represented as:

\[C_e = \frac{d\rho}{d\Delta x} = \frac{d\varphi_e}{d\Delta x} \cdot \frac{d\varphi_e}{d\rho} \cdot \frac{dx}{dz} = \frac{p_e^2}{p_e^2 + 4\pi \varepsilon_S} \quad (15)\]

where and is the free charge volume and surface density respectively; \(z\) is the DEL thickness; is the interface barrier jump; is the DEL dielectric capacitance.

The conclusion could have been immediately drawn, that substances with high electrical conductivity should be used as the electrode material.

The second additive component in equation (14) is written in the following form:

\[\frac{d\rho}{d\varphi_d} = \frac{d\rho}{d\varphi_d} \cdot \frac{d\varphi_d}{d\rho} = \varepsilon \frac{d\varphi_d}{d\varphi} = C_d \quad (16)\]

where \(\frac{d\rho}{d\varphi_d} = \varepsilon\) – is the const, i.e., the effective dielectric constant, averaged throughout the dipole layer. Equation (16) suggests that the DEL capacitance increases with the dipoles number and DEL dipole moment value increase, which ensures \(\varepsilon\) and factor \(\frac{d\varphi_d}{d\varphi}\) increase.

4. Conclusions

1. It has been shown that the mechanism of CSC and UCS electrical energy accumulation is connected with the bound and free charges. The amount of accumulated energy is defined primarily by polarization effects in the system and is expressed by the formula: \(A = PE\).

2. The interface barrier jump, which determines the operating voltage of the CSC and electrolytic UCS (supercondensers) to a precision of a certain constant is determined by the electron release into environment work - \(\Delta X\) [10, 13]. CSC and electrolytic UCS energy intensity is determined by polarization processes and operating voltage, which depends on the barrier jumps on electrode materials.

3. To improve the CSC energy intensity, the chemically active substance should be nanostructured to increase the number of dipole moments and their size, and electrode materials should ensure stable maintaining of initial nanostructure during operation. One of the options is the use of a highly porous matrix when producing electrode materials. In this case, thin film technology allows the creation of hybrid UCS in which CSC and UCS properties are integrated. Lately this area is progressing actively and shows excellent results regarding energy intensity (energy intensity of 220 to 250 W h/kg).

4. Since CSC and UCS employ physically the same mechanism for electrical energy accumulation, it is thus possible to combine design solutions and develop a unified CSC and UCS electrode material based on the thin-film technology. In this case, it is possible to increase the specific energy intensity of the energy storage unit along with its specific capacity growth in the framework of a single design solution.
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