



Mathematical Modelling, Design and Optimization of Symmetric Electrochemical Supercapacitors from Layered Materials

Presented By

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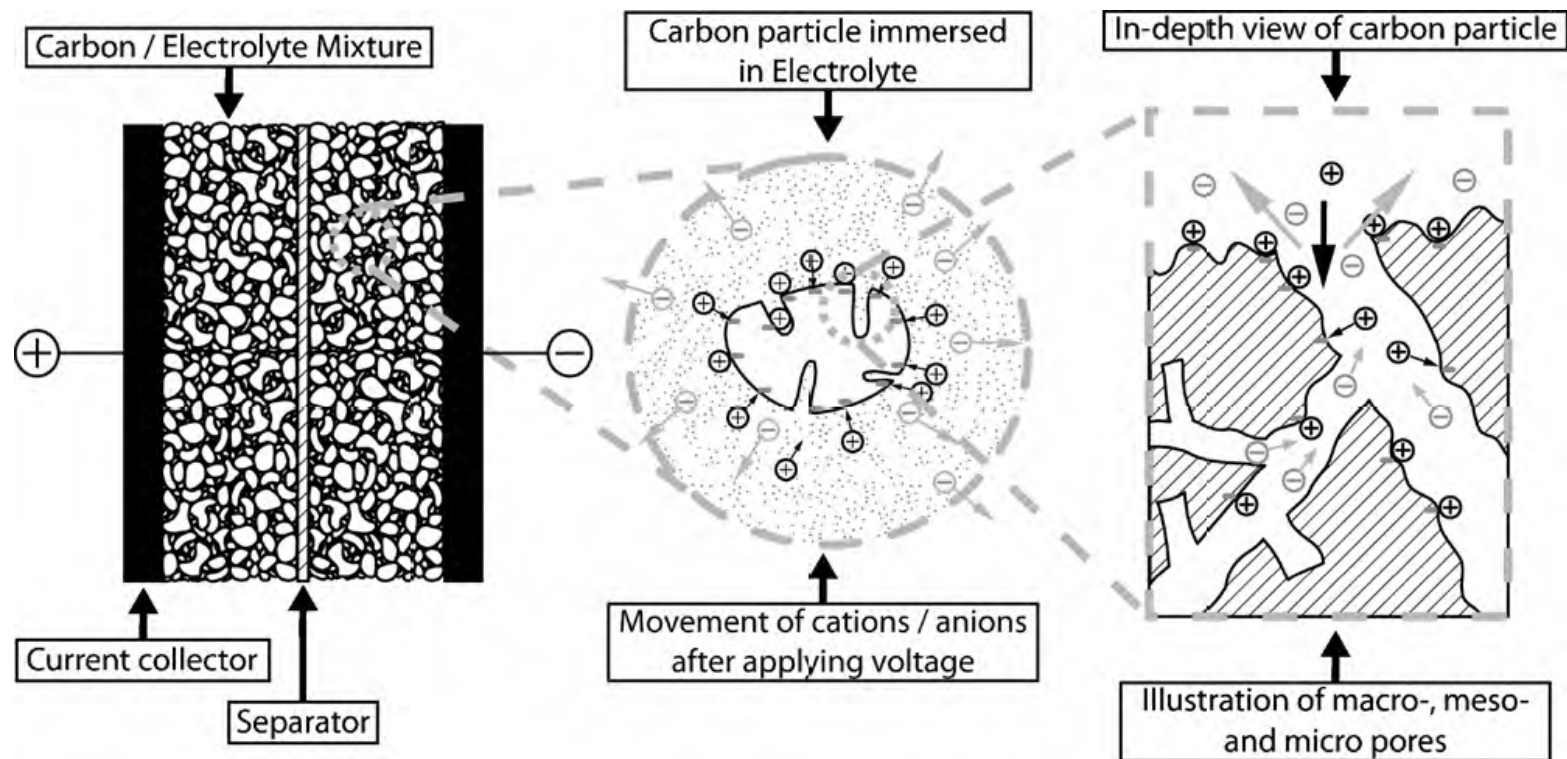
PRESENTATION OUTLINE

- ❖ Objectives
- ❖ Overview
- ❖ Mathematical Models
- ❖ Results
- ❖ Discussion of Results
- ❖ Conclusions

OBJECTIVES

- To develop a mathematical description of ESs subject to characteristic parameters of cell layers;
- To build theoretical basis for calculations and improvement of energy and other parameters of ESs;
- To provide ideal alternative to time-consuming numerous experiments for design and optimization of ESs cell;
- To optimize specific energy, power density, etc, of ESs subject to characteristic properties of its layers;
- To develop an Optimal Process Design of the ESs Cell.

ILLUSTRATION OF THE BASIC COMPONENTS AND DESIGN OF AN EDLS



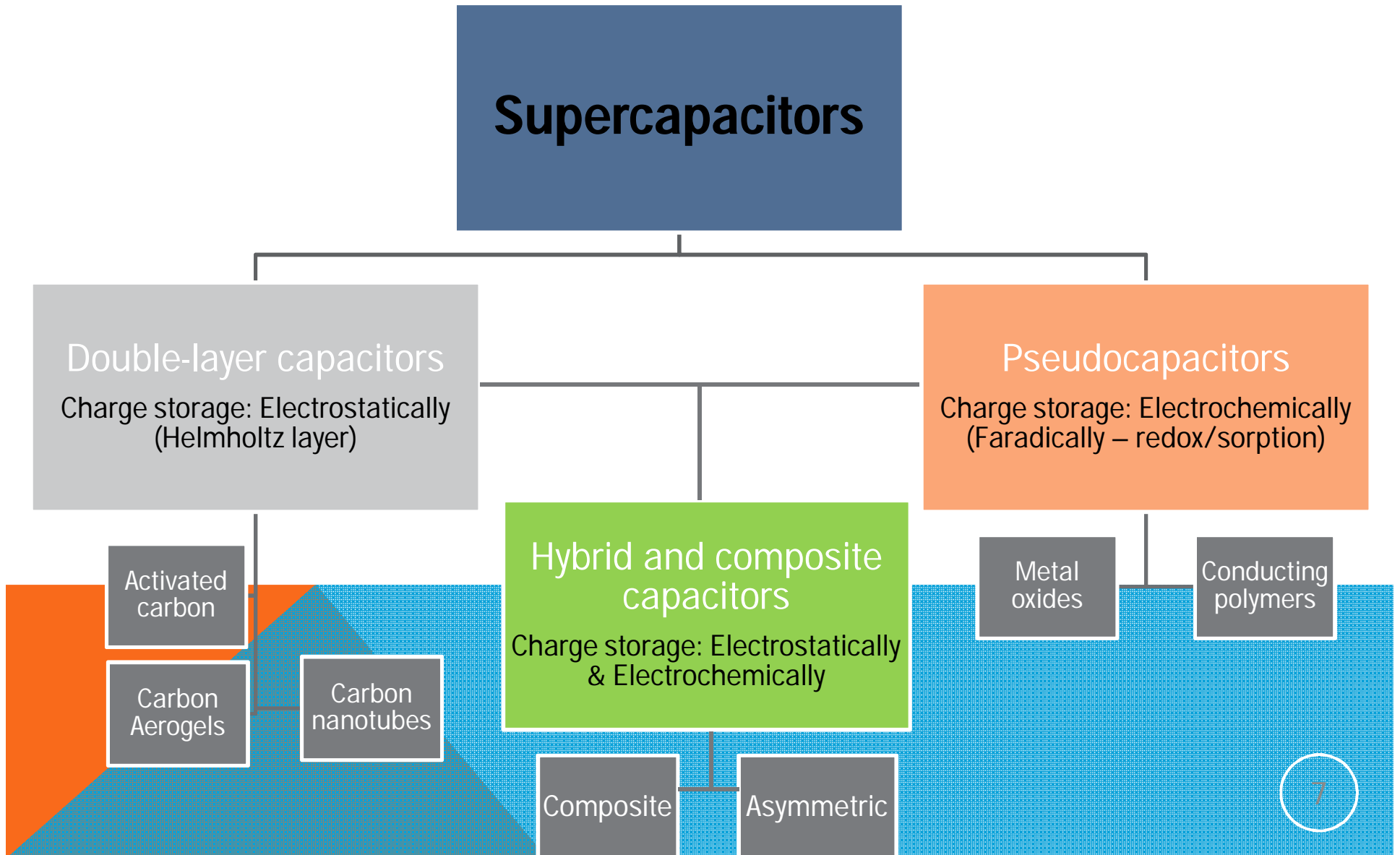
Advantages

- Long life: It works for large number of cycle without wear and aging.
- Rapid charging: it takes seconds to charge completely
- High power storage: It stores huge amount of energy in a small volume.
- Faster release: Release the energy much faster than battery.
- Low toxicity of materials used.
- High cycle efficiency: 95% or more (low ESR).

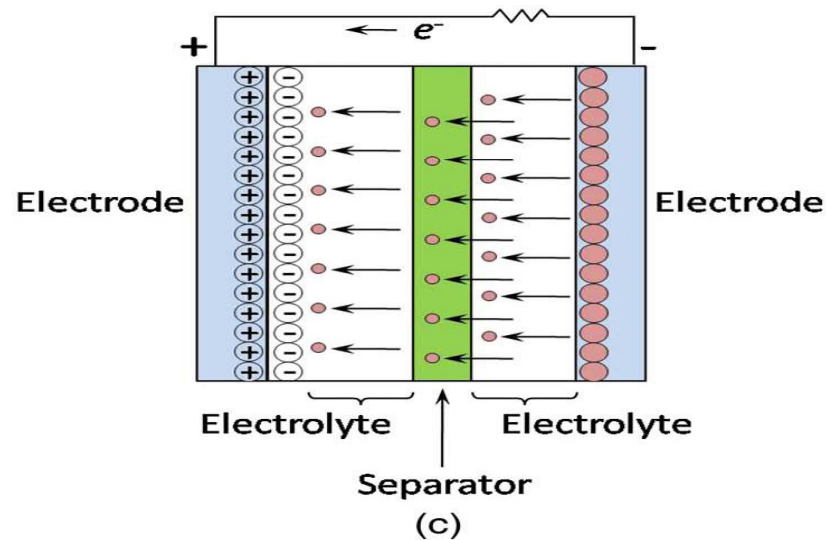
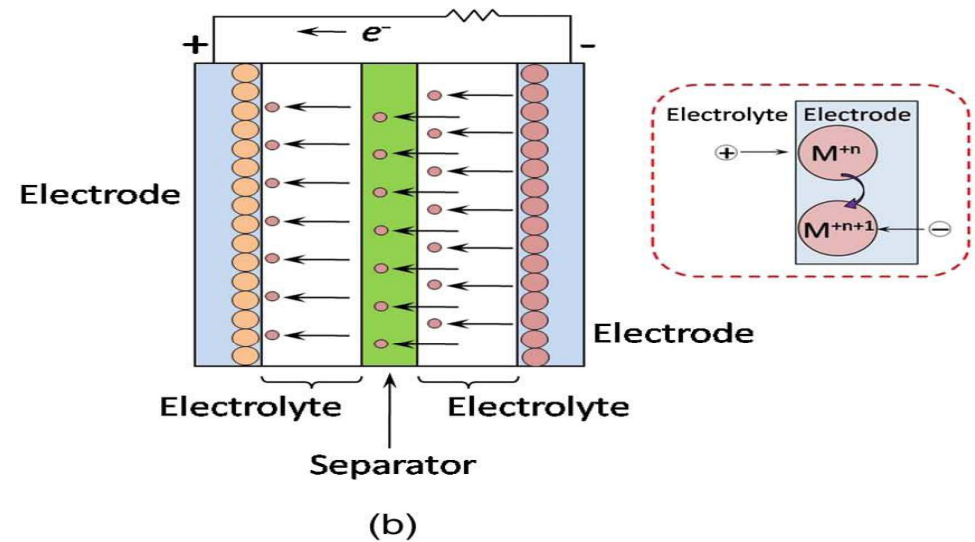
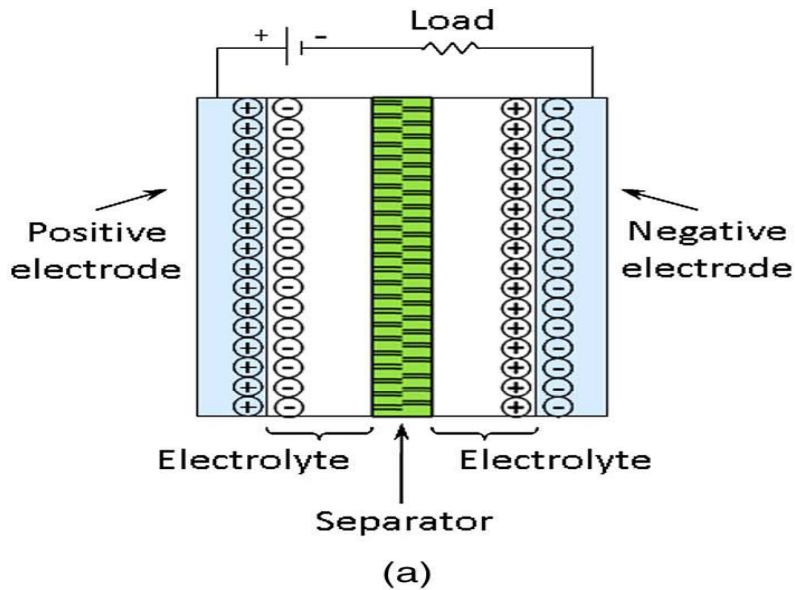
Disadvantages

- ❖ They have low energy density
- ❖ Individual cell shows low voltage
- ❖ They have high self-discharge as compared to battery.
- ❖ Voltage balancing is required when more than three capacitors are connected in series.
- ❖ The voltage varies with the energy stored.
- ❖ To effectively store and recover energy requires sophisticated electronic control and switching equipment.

TYPES OF SUPERCAPACITORS



SCHEMATIC REPRESENTATION OF SUPERCAPACITOR TYPES: (A) EDLS TYPE; (B) PSEUDOCAPACITORS TYPE; (C) HYBRID CAPACITOR TYPE (THE FIGURE IS NOT TO SCALE)



HOMOGENEOUS (SYMMETRIC) SUPERCAPACITORS WITH ONLY EDLS ELECTRODES.

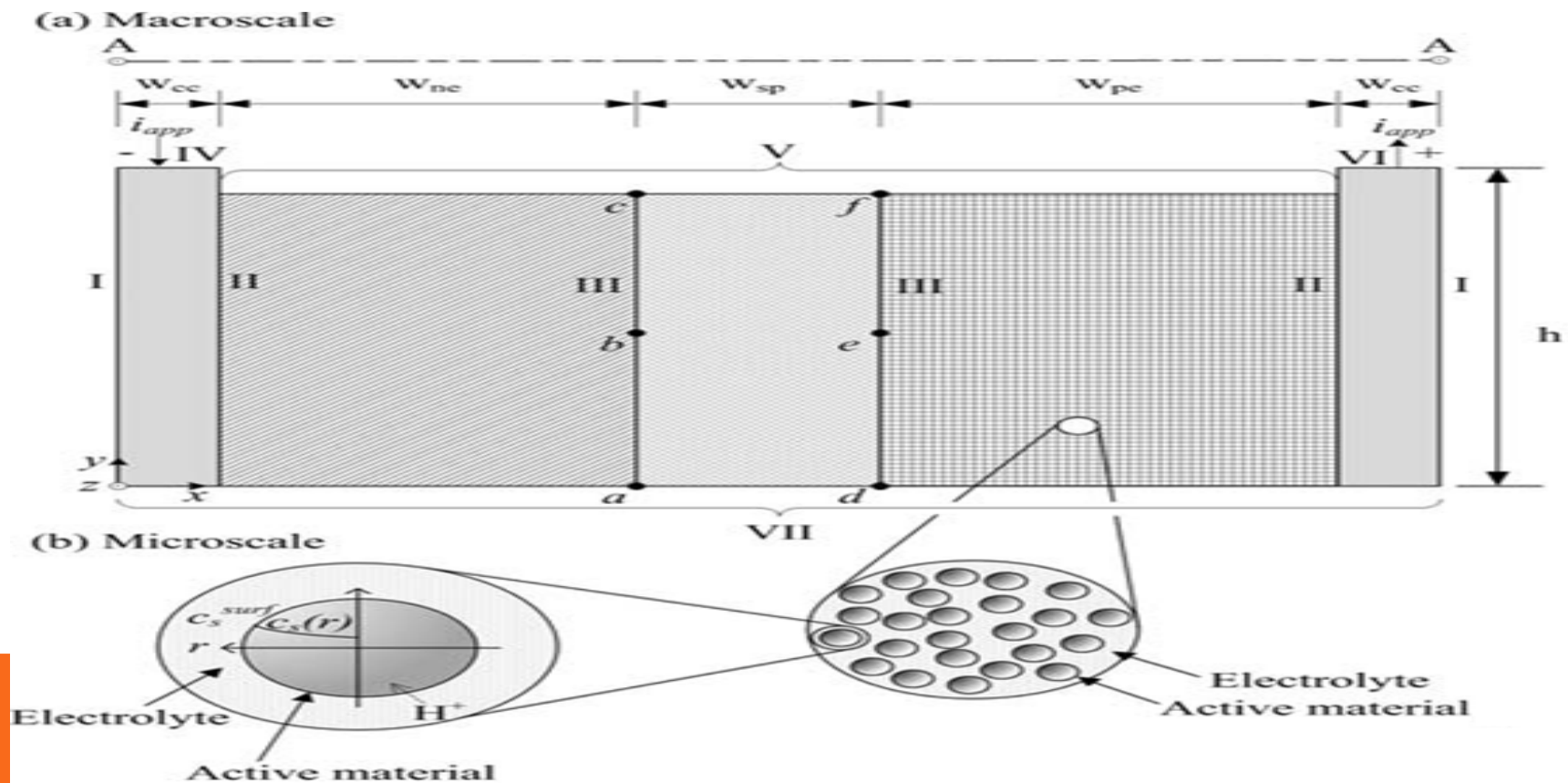
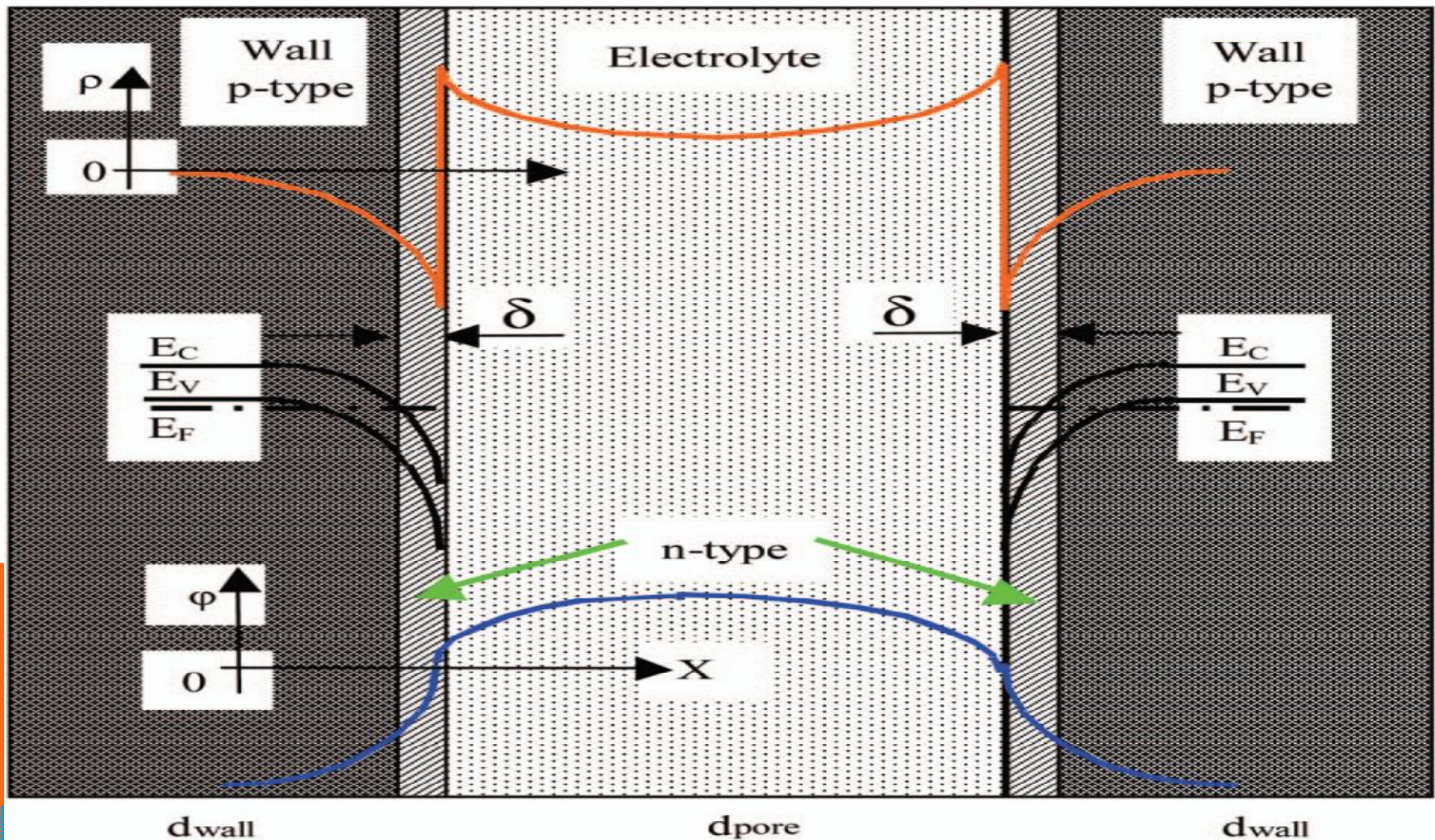


Figure 1. A symmetric supercapacitors cell with only EDL electrodes showing (a) various functional layers on the macroscale, and (b) the active material on the electrodes on the microscale.

Distributions of electric charge and potentials in the walls of cylindrical shaped pores and in the electrolyte which is inside the pores of the negative electrode with p-type conductivity.



THE MODEL EQUATIONS WITHOUT SELF-DISCHARGES TERM

$$\frac{\partial \varphi_{ne}(x, t)}{\partial t} = \beta^2 \frac{\partial^2 \varphi_{ne}(x, t)}{\partial x^2} \quad 1$$

$$\beta^2 = \frac{\alpha_1 \alpha_2}{C_V (\alpha_2 + \alpha_1)} \quad 2$$

$$J_{VR}(x, t) = J_{VR1}(x, t) = J_{VR2}(x, t) \quad 3$$

The boundary conditions of this task during the capacitor discharge are as follows:

$$J_1(0, t) = -\alpha_1 \frac{\partial \varphi_{ne}(x, t)}{\partial x} \Big|_{x=0} = J_0 \quad 4$$

$$J_2(w, t) = \alpha_2 \frac{\partial \varphi_{ne}(x, t)}{\partial t} \Big|_{x=w_{ne}} = J_0 \quad 5$$

and the initial condition is as follows:

$$\varphi_{ne}(x, t) \Big|_{t=0} = \varphi_{ne}^{0-} \quad 6$$

The boundary conditions of this task during the capacitor charge are as follows:

$$J_1(0, t) = \alpha_1 \frac{\partial \varphi_{ne}(x, t)}{\partial x} \Big|_{x=0} = J_0 \quad 7$$

$$J_2(w, t) = -\alpha_2 \frac{\partial \varphi_{ne}(x, t)}{\partial x} \Big|_{x=w_{ne}} = J_0 \quad 8$$

and the initial condition is as follows:

$$\varphi_{ne}(x, t) \Big|_{t=0} = \varphi_{ne}^{0+} \quad 9$$

Solutions of the Supercapacitors Models without Self-discharges

Solving equation 1 with the boundary and initial conditions, we obtain equation 10 below:

$$\varphi_{ne}(x,t) = \varphi_{ne}^{0+} \pm \frac{J_0 t}{w_{ne} C_V} \pm \frac{J_0 C_V}{w_{ne} C_V} \left[\frac{(\alpha_2 + \alpha_1)}{2\alpha_1\alpha_2} x^2 - \frac{w_{ne} x}{\alpha_2} + \frac{w_{ne}^2 (2\alpha_2 - \alpha_1)}{6\alpha_1\alpha_2} - \frac{2w_{ne}^2}{\pi^2 n^2} \right. \\ \left. \sum_{n=1}^{\infty} \left(\frac{1}{\alpha_1} + \frac{(-1)^n}{\alpha_2} \right) \ell^{\frac{\beta^2 n^2 \pi^2 t}{w_{ne}^2}} \cos \left(\frac{n\pi x}{w_{ne}} \right) \right] \quad 10$$

where the sign

$$\frac{J_0}{w_{ne} C_V} < 0 \quad (\text{sign "-"} \text{ represents the process of the supercapacitors charge})$$

$$\frac{J_0}{w_{ne} C_V} > 0 \quad (\text{sign "+" represents the process of the supercapacitors discharge.})$$

VOLTAGE OF THE SUPERCAPACITORS WITHOUT SELF-DISCHARGE TERM

The voltage $V(x,t)$ of the supercapacitors as a function of its thickness and time of charge and discharge is given as:

$$V(x,t) = -\frac{1}{2}\varphi_{ne}(w_{ne},t) - \frac{1}{2}\varphi_{ne}(0,t) \quad 11$$

On substituting $x = w_{ne}$ and $x = 0$ into equation 10, equation 11 will be as follow:

$$V(w_{ne},t) = V_{0_{\pm}} \pm \frac{J_0}{w_{ne}C_V} \left\{ t + \frac{C_V w_{ne}^2 (\alpha_2 + \alpha_1)}{2\alpha_2\alpha_1} X \left[\frac{1}{6} - \frac{1}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \ell \left(\left(\frac{2n\pi}{w_{ne}} \right)^2 \left[\frac{\alpha_2 \alpha_1 t}{C_V (\alpha_2 + \alpha_1)} \right] \right) \right] \right\} \quad 12$$

Where $V_{0_{\pm}} = -\varphi_{ne}^{0_{\pm}}$ and the sign $\frac{J_0}{w_{ne}C_{ne}} < 0$ (sign "-") represents the process of the supercapacitors discharge

$\frac{J_0}{w_{ne}C_V} > 0$ (sign "+") represents the process of the supercapacitors charge.

When the effective conductivities of the electrode and the electrolyte are the same, that is, $\alpha_1 = \alpha_2 = \alpha$ equation 12 has the following expression

$$V(w_{ne}, t) = V_{0_{\pm}} \pm \frac{J_0}{w_{ne} C_V} \left\{ t + \frac{C_V w_{ne}^2}{\alpha} X \left[\frac{1}{6} - \frac{1}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \ell \left(\left(\frac{2n\pi}{w_{ne}} \right)^2 \left[\frac{\alpha t}{2C_V} \right] \right) \right] \right\} \quad 13$$

Electromotive force (emf) of supercapacitors is determined as

$$U_S(w_{ne}, w_{sp}, w_{pe}, \beta, C_V, t) = \varphi_{pe}(0, t) - \varphi_{ne}(0, t) \quad 14$$

From Equation 31 we obtain an analytical expression for emf of the supercapacitors during its charge and discharge by constant current as:

$$U_S(d, t) = U_{S0} \pm \frac{J_0}{C_V} w_{S1} \left\{ t + C_V w_{S2} \left[\frac{(2\alpha_2 - \alpha_1)}{6\alpha_1\alpha_2} - \frac{2}{\pi^2} w_{S2} \sum_{n=1}^{\infty} \frac{1}{n^2} \ell \left(\left(\frac{2n\pi}{w_{S1}} \right)^2 \left[\frac{\alpha_2 \alpha_1 t}{C_V(\alpha_2 + \alpha_1)} \right] \right) \right] \right\} \quad 15$$

where $U_{S0} = \varphi_{pe}^{0+} - \varphi_{ne}^{0+}$ is the emf of the supercapacitors at $t = 0$;

$$w_{S1} = \left(\frac{1}{w_{pe}} - \frac{1}{w_{ne}} \right) \quad \text{and} \quad w_{S2} = (w_{pe} - w_{ne})$$

VOLTAGE OF THE SUPERCAPACITORS WITHOUT SELF-DISCHARGE TERM CONT.

Because supercapacitors has specific internal resistance, $\rho_{\text{int}} (\Omega \text{cm}^2)$, the supercapacitors voltage during the charge and discharge is expressed by the formula:

$$U(w_e, t) = U_0 \pm J_0 \rho_{\text{int}} \pm \frac{J_0 w_{s1}}{C_V} \left\{ t + C_V w_{s2} \left[\frac{(2\alpha_2 - \alpha_1)}{6\alpha_1 \alpha_2} - \frac{2w_{s2}}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \ell \left(\frac{2n\pi}{w_{s1}} \right)^2 \left[\frac{\alpha_2 \alpha_1 t}{C_V (\alpha_2 + \alpha_1)} \right] \right] \right\} \quad 16$$

Recall that the effective conductivities of the electrodes α_1 and the electrolytes α_2 are respectively defined by equations 17 and 18

below :

$$\alpha_1 = \sigma_{ne}^s + 2D_e C_V \quad 17$$

$$\alpha_2 = \sigma_{ne}^l + 2D_+ C_V \quad 18$$

RESULTS

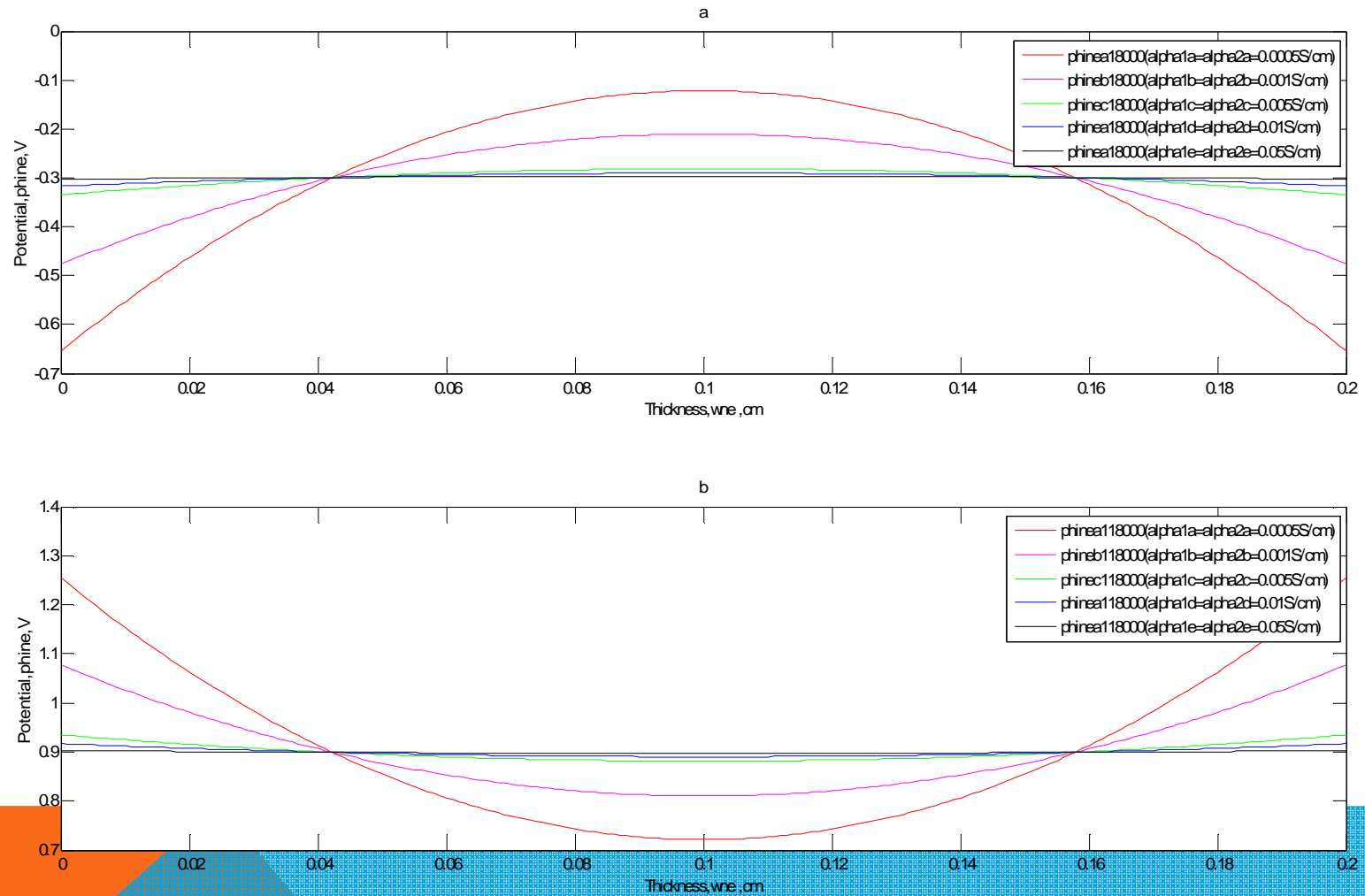


Figure 2. Distribution of potential of the negative electrode as a function of position after (a) 5 h charge and (b) 5 h discharge by constant current of supercapacitors with different parameters of α_1 and α_2

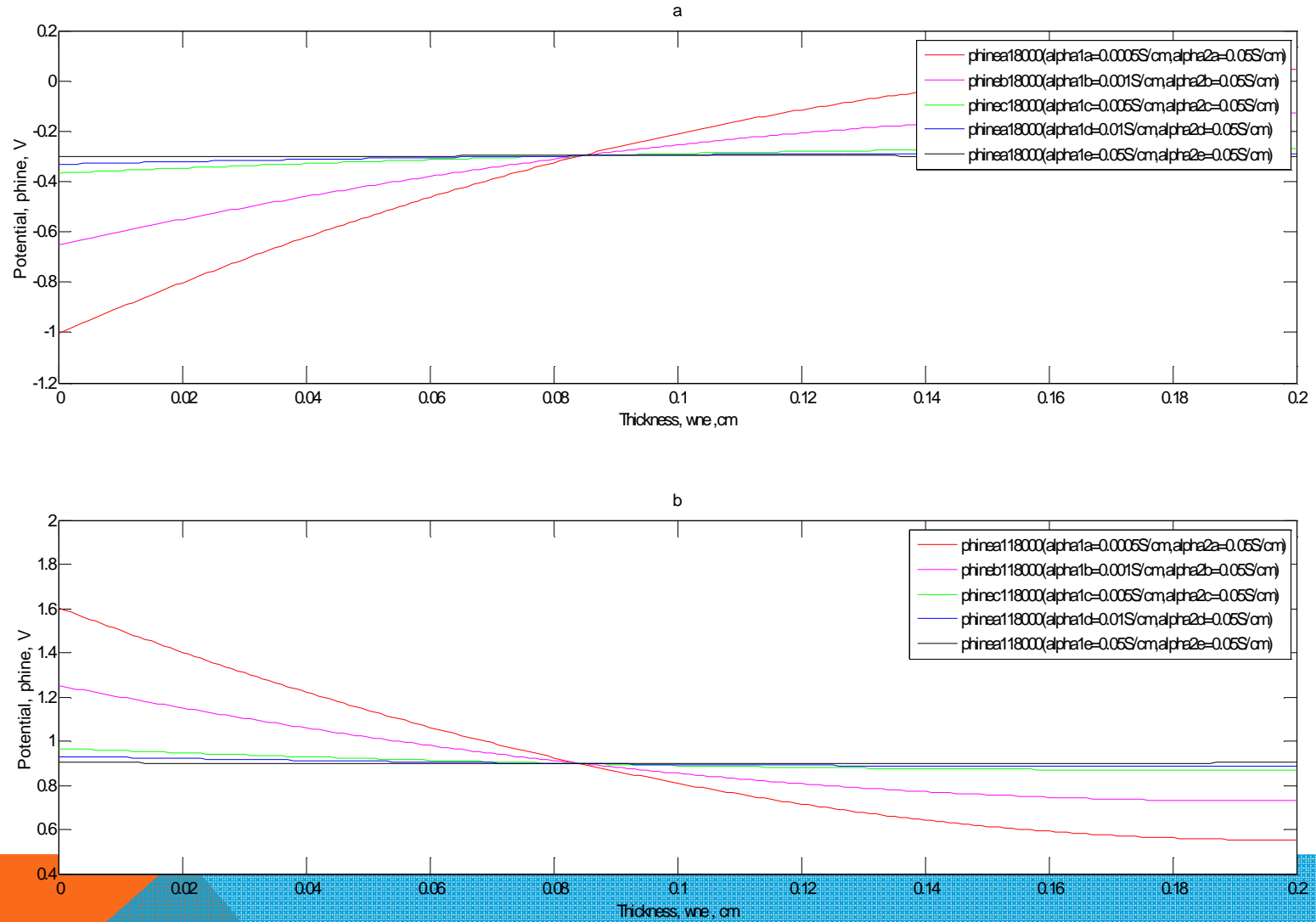


Figure 3. Distribution of potential of the negative electrode as a function of position after (a) 5 h charge and (b) 5 h discharge by constant current of supercapacitors with different parameters of α_1

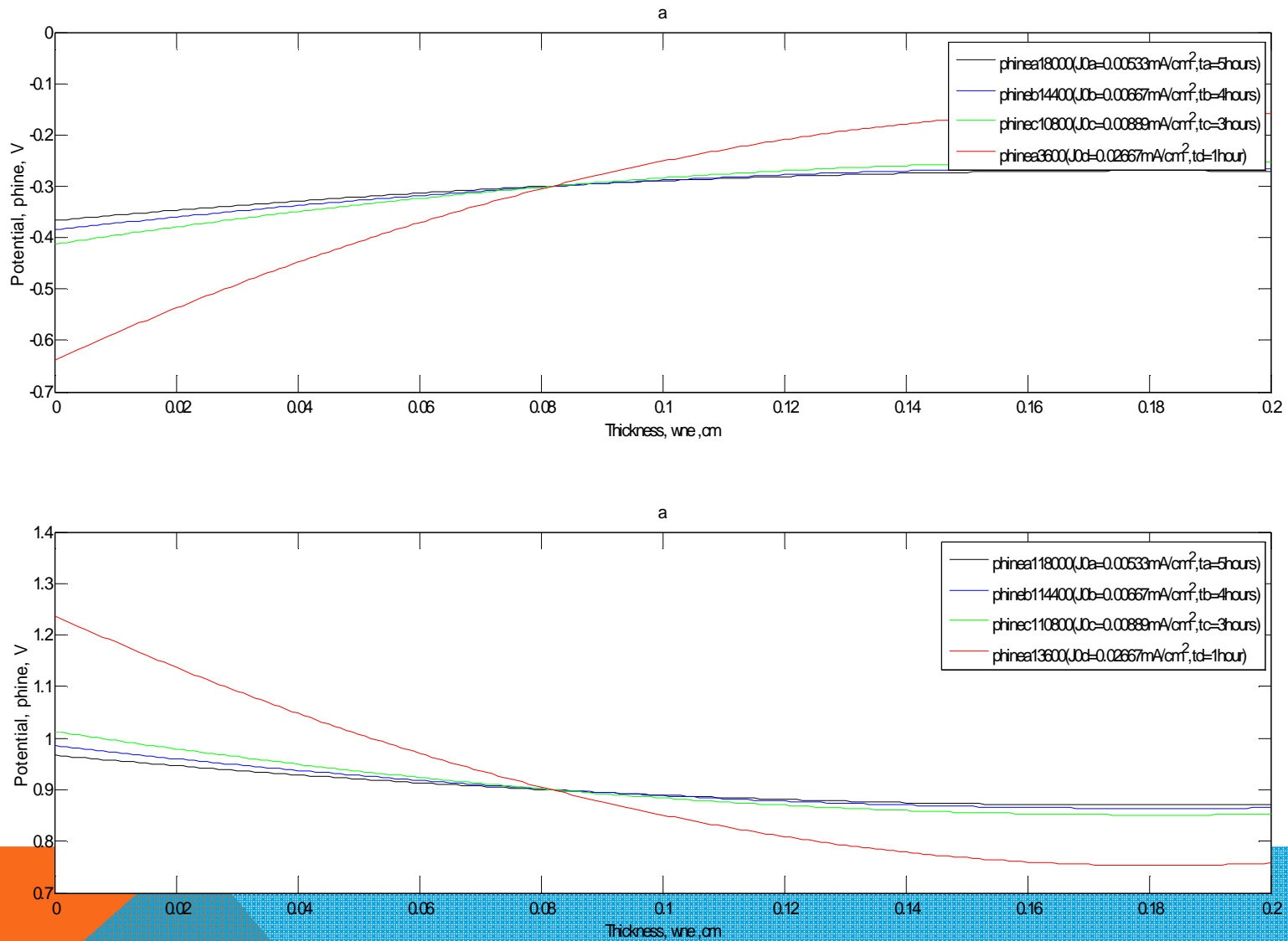


Figure 4. Distribution of potential of negative electrode as a function of position during (a) charge and (b) discharge of supercapacitors by constant current of different densities and different charge and discharge time.

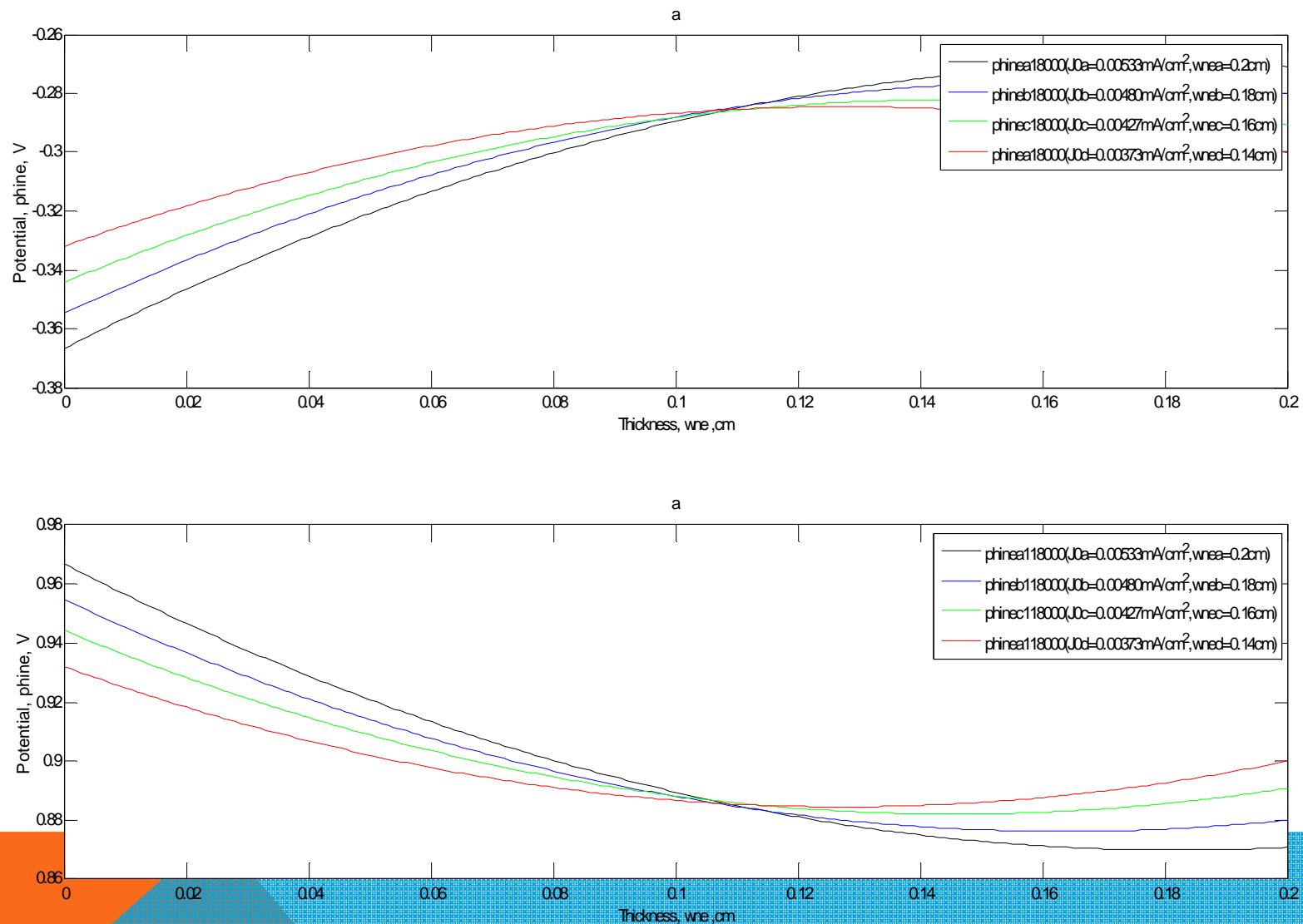


Figure 5. Distribution of potential of negative electrodes as a function of position at (a) 5 h charge and (b) 5 h discharge by constant current of supercapacitors with different thickness of negative electrode.

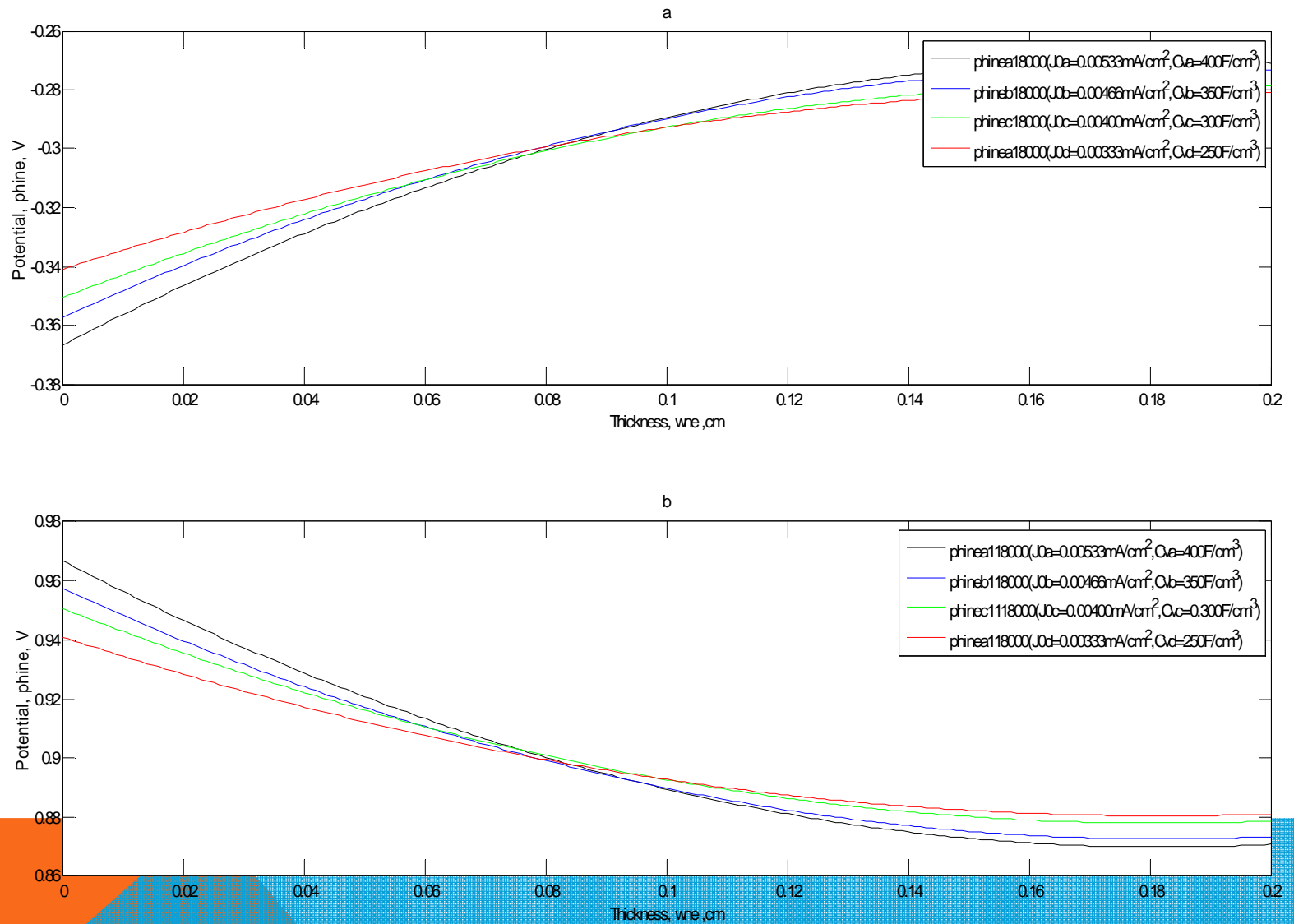


Figure 6. Distribution of potential of negative electrode as a function of position at (a) 5 h charge and (b) 5 h discharge of supercapacitors with different values of specific capacitance by constant current of different densities.

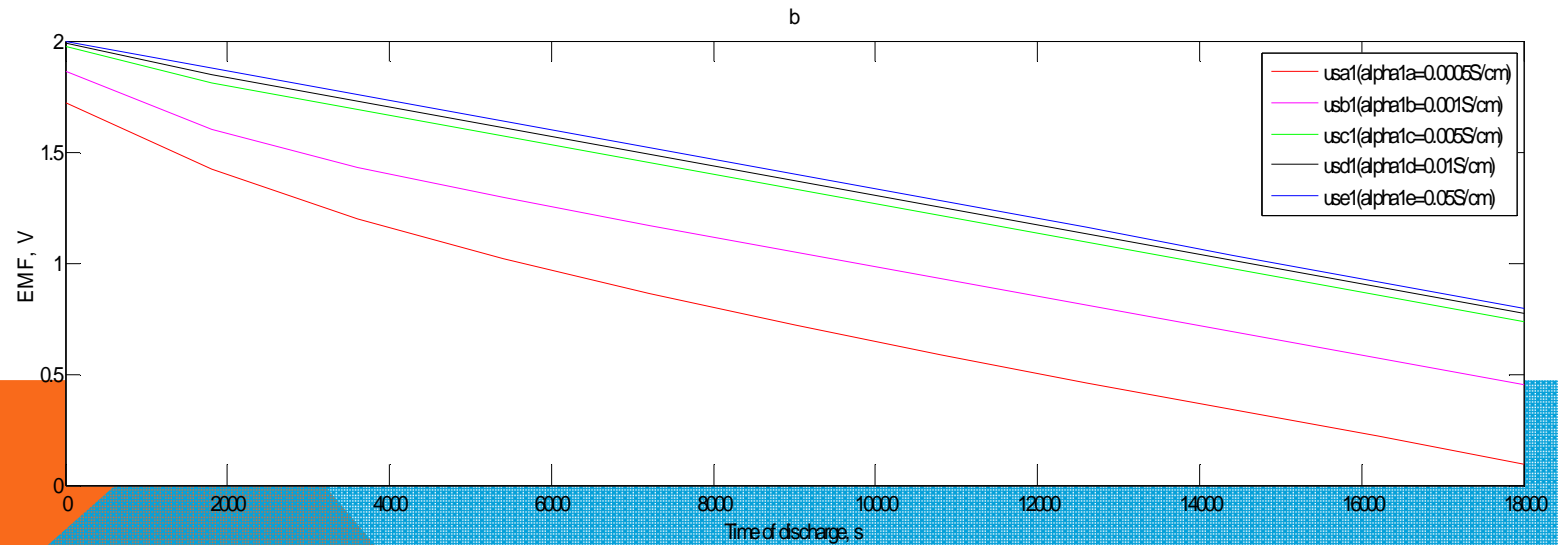
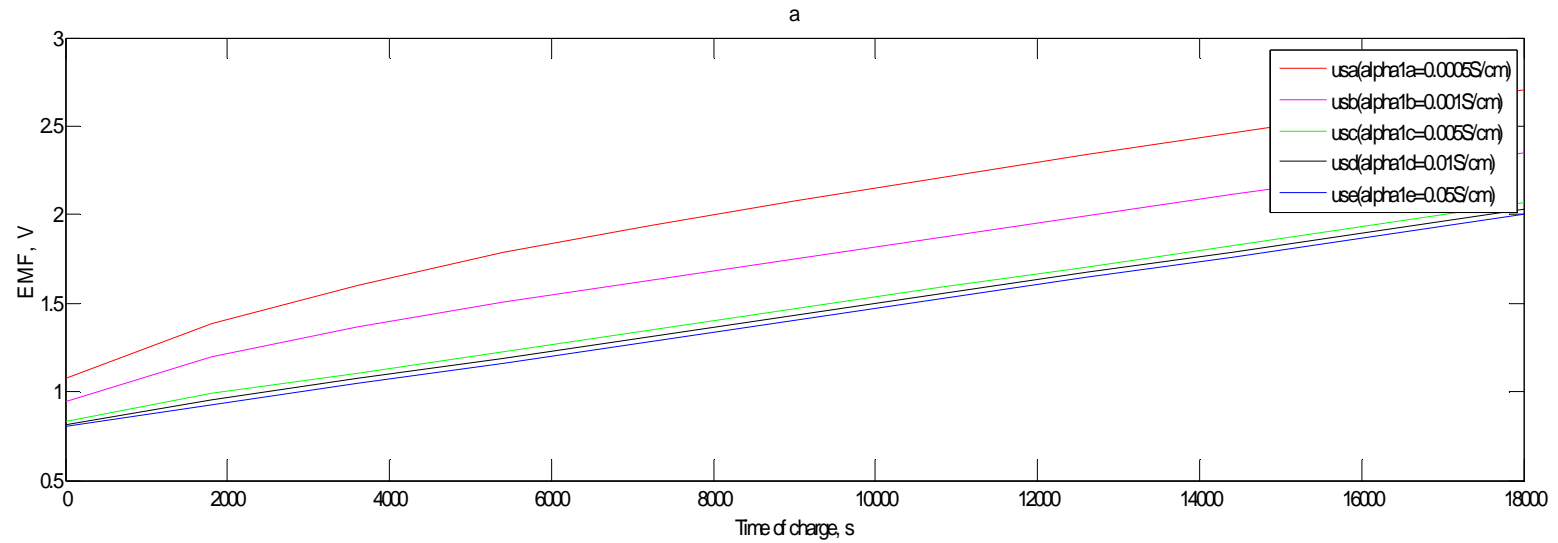


Figure 7. Capacitor dependence of emf on time during (a) 5 h charge and (b) 5 h discharge with different α_1 and constant current.

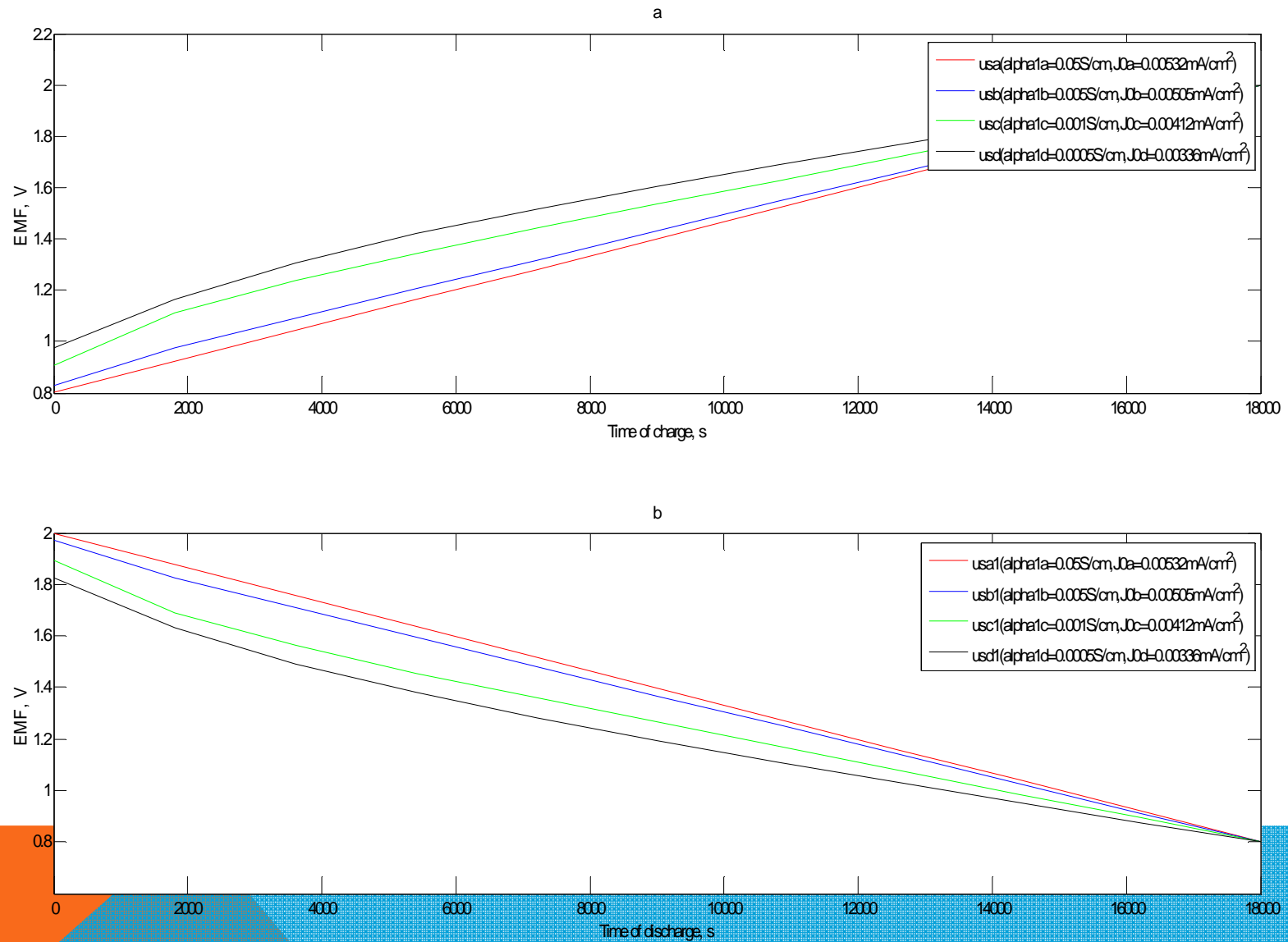


Figure 8. Supercapacitors emf dependence on time of a 5 h charge and b 5 h discharge with different parameters during charge to emf = 2 V and discharge to emf = 0.8 V.

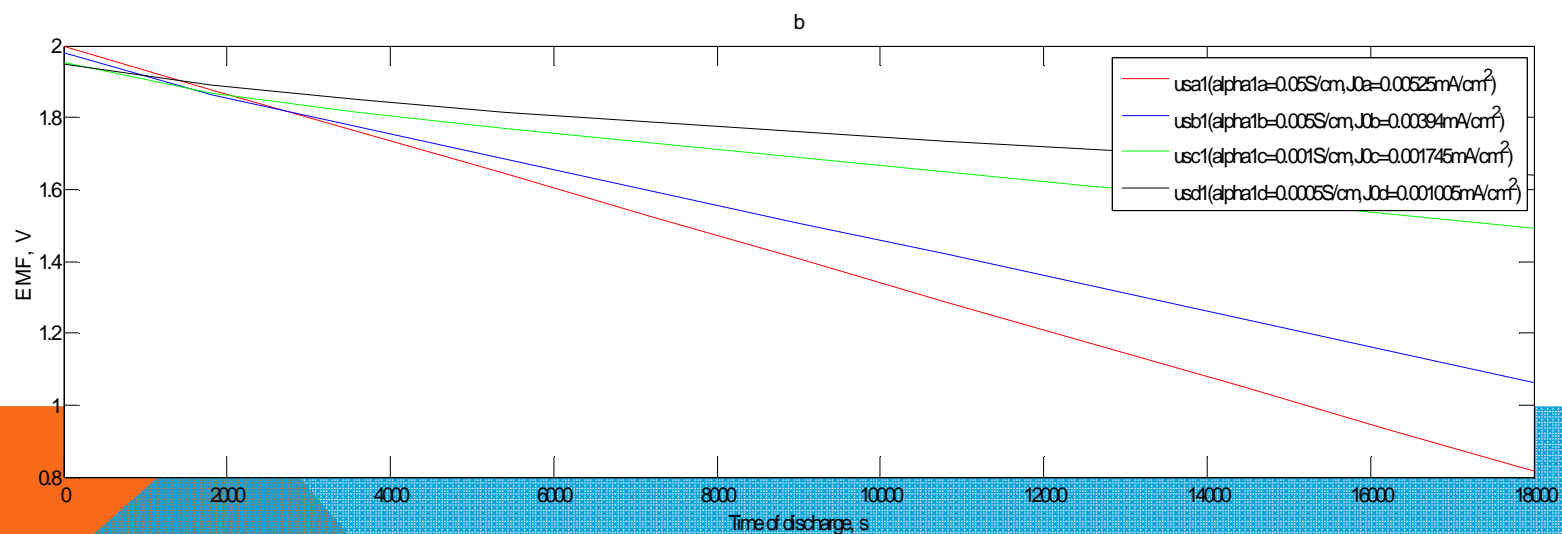
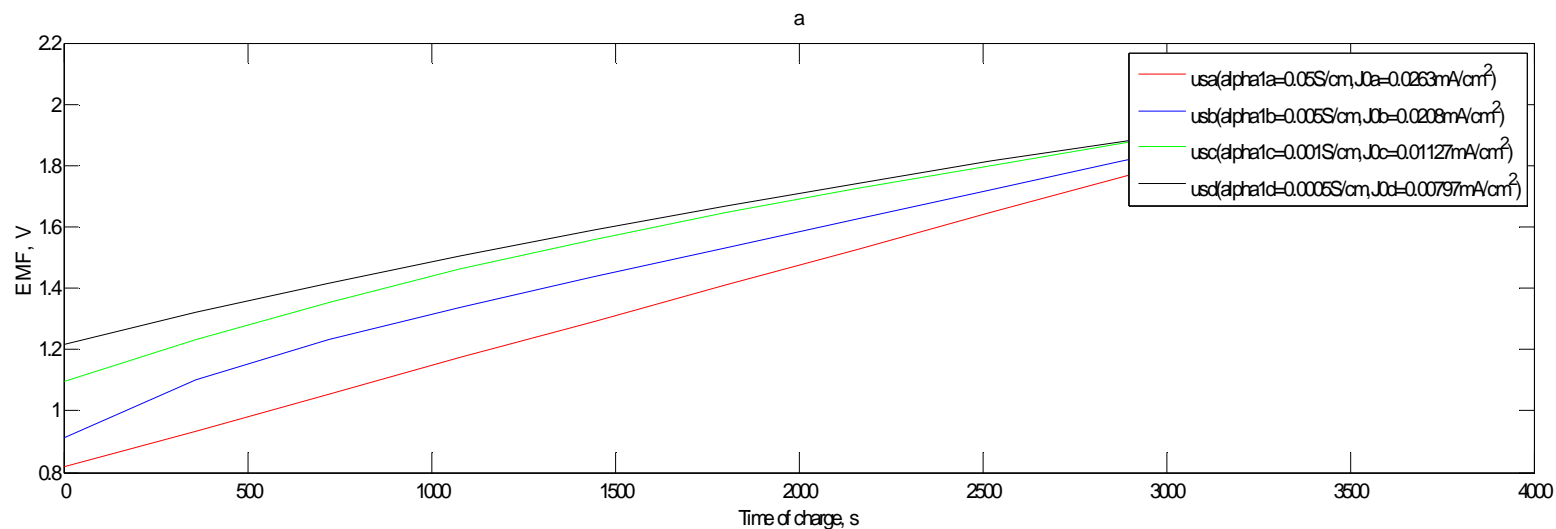


Figure 9. Capacitor emf dependences on the time of (a) 1 h charge and (b) 5 h discharge with different parameters during charge emf = 2 V and discharge to emf = 0.8 V.

Table 1. Parameters of the Supercapacitors during charge and discharge in mode I and II

			(S/cm) Alpha1 = Alpha2 = Alpha							
			Mode I				Mode II			
S/N	parameter	units	0.0005	0.001	0.005	0.05	0.0005	0.001	0.005	0.05
1	I_{ch}	A	21.134	25.915	31.76	33.46	50.13	70.89	130.83	165.427
2	Q_{ch}	Ah	105.67	129.574	158.82	167.31	50.13	70.89	130.83	165.427
3	E_{Sch}	Wh	165.99	196.83	227.32	234.576	80.258	113.26	198.2	233.12
4	E_{Sch}^{eff}	Wh	127.22	164.736	217.24	233.989	56.617	80.258	166.793	230.237
5	E_{ch}^{Rpol}	Wh	38.77	32.094	10.08	0.587	23.641	32.463	31.407	2.883
6	U_{Sch}^{ap}	V	1.556	1.727	1.936	1.997	1.159	1.307	1.736	1.9835
7	E_{Sch}^{ap}	Wh	124.48	163.71	217.22	233.987	49.15	74.66	165.89	230.23
8	E_{ch}^{dpol}	Wh	2.74	1.026	0.02	0.002	7.467	6.137	0.903	0.007
9	E_{ch}^R	Wh	4.26	6.406	9.625	10.68	4.7945	9.587	32.655	52.208
10	E_{ch}	Wh	170.25	203.24	236.94	245.26	85.053	122.847	230.855	285.328
11	I_{dis}	A	13.33	20.065	30.066	33.4	6.32	10.976	24.78	30.02
12	Q_{dis}	Ah	66.67	100.3	150.33	167.0	31.6	54.88	123.91	165.11
13	E_{Sdis}	Wh	71.319	117.40	201.21	233.15	29.346	55.014	154.082	229.486
14	E_{Sadis}	Wh	37.728	27.07	7.068	0.252	16.337	13.886	5.7386	0.3082
15	E_{dis}^{Rpol}	Wh	15.433	19.24	8.942	0.585	3.467	5.760	6.0694	0.4358
16	U_{Sdis}^{ap}	V	1.079	1.0094	0.8607	0.8022	0.9325	0.9145	0.8495	0.80226
17	E_{dis}^{ap}	Wh	36.64	26.48	7.045	0.246	16.04	13.72	5.706	0.254
18	E_{dis}^{dpol}	Wh	1.087	0.59	0.023	0.006	0.297	0.166	0.0326	0.0544
19	E_{dis}^R	Wh	1.696	3.84	8.479	10.64	0.381	1.149	5.857	8.596
20	E_{dis}	Wh	69.62	113.56	192.73	222.51	28.965	53.865	148.225	220.89
21	Q_{Sadis}	Ah	39.0	29.27	8.49	0.31	18.53	16.01	6.92	0.317
22	η_{E1}	%	40.89	55.87	81.34	90.72	34.055	43.847	64.207	77.416
23	η_{E2}	%	62.41	68.9	84.315	90.71	52.914	55.024	66.678	77.505
24	δ_{ERpol}	%	31.83	25.24	7.9	0.477	31.87	31.114	16.246	1.163
25	δ_{ER}	%	3.498	5.04	7.51	8.6928	6.085	8.740	16.683	21.31
26	δ_{Edpol}	%	2.247	0.795	0.422	0.003	9.128	5.126	0.405	0.02

CONCLUSIONS

The energy, capacity, power parameters, energy efficiency of charge–discharge cycles of the capacitors will depend on:

- ❖ type and value of the effective conductivity of the solid matrixes of electrodes with DEL
- ❖ the effective conductivity of electrolyte
- ❖ thickness and specific capacitance of electrodes
- ❖ values of charge and discharge currents of the supercapacitors
- ❖ and the time of charge and discharge of supercapacitors.

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COMMENTS

CONTRIBUTIONS

Questions



Mathematical modelling, design, and optimization of electrochemical capacitors from layered materials
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28