



The effects of self-discharge on the performance of symmetric electric double layer capacitors: Insights from mathematical modeling and simulation.

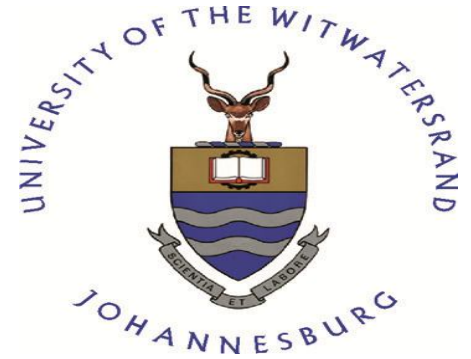
Presented By

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The effects of self-discharge on the performance of symmetric electric double layer capacitors: insights from mathematical modeling and simulation by Ike, I. S.; Iakovos, S.; Iyuke, S.; Ozoemena, K. I. and Sigalas, I. J. is licensed under a [Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License](https://creativecommons.org/licenses/by-nc-nd/4.0/).

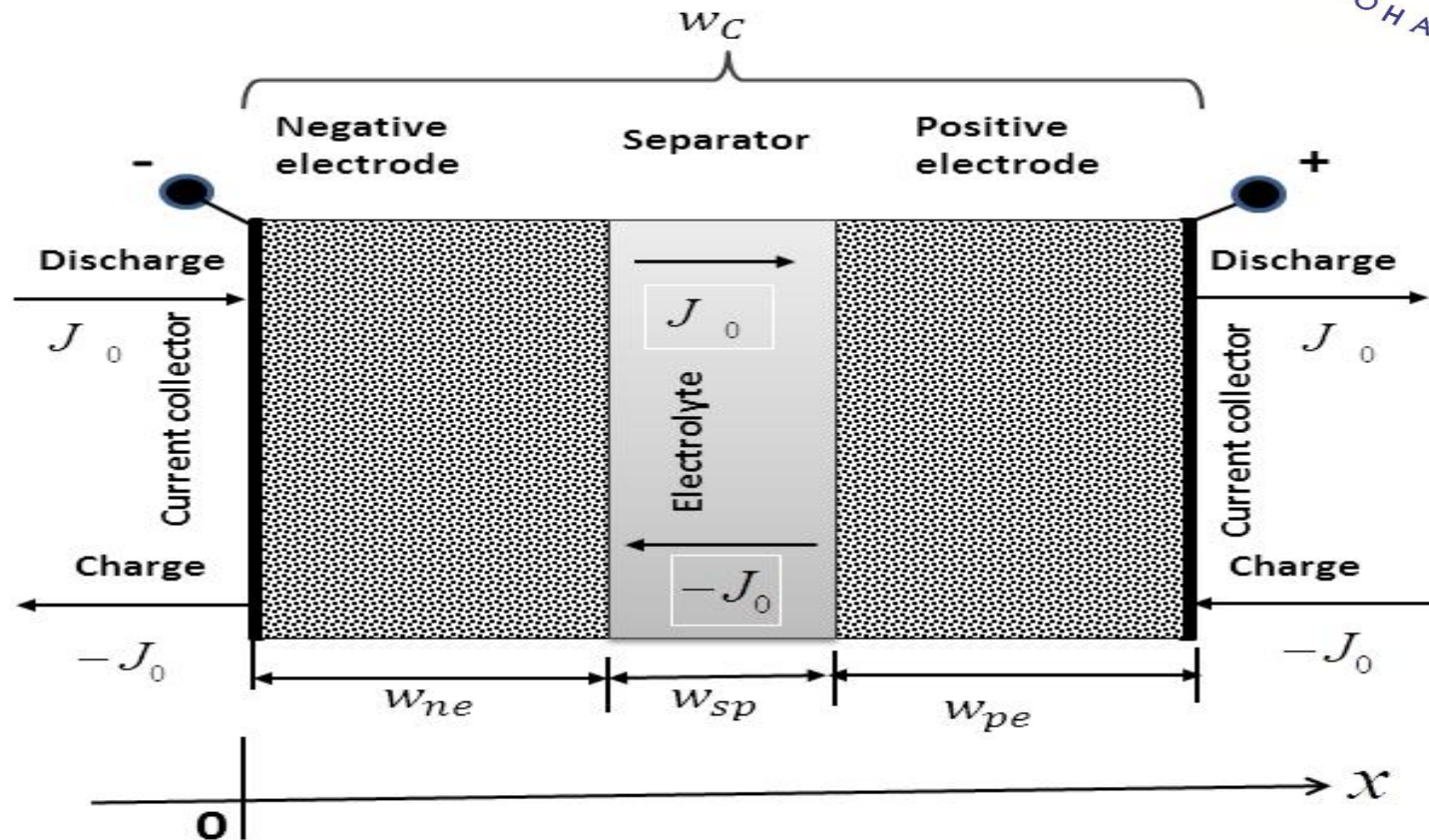


PRESENTATION OUTLINE

- Overview
- Self-discharge Mechanisms
- Mathematical Models
- Results
- Discussion of Results
- Conclusions



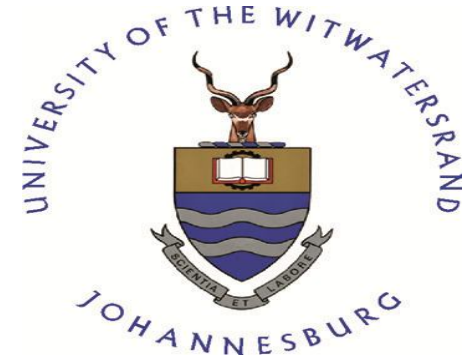
OVERVIEW



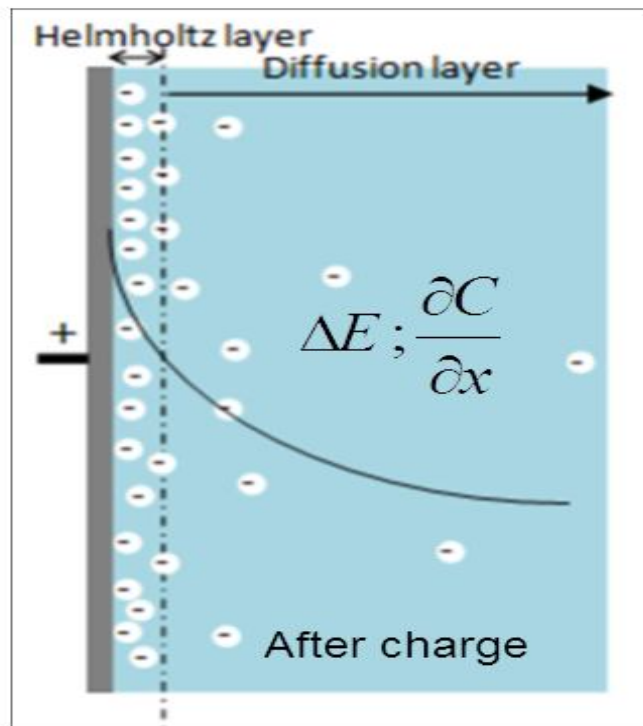
A symmetric electrochemical capacitor cell with only electric double layer, EDL electrodes showing various functional layers on the macroscale



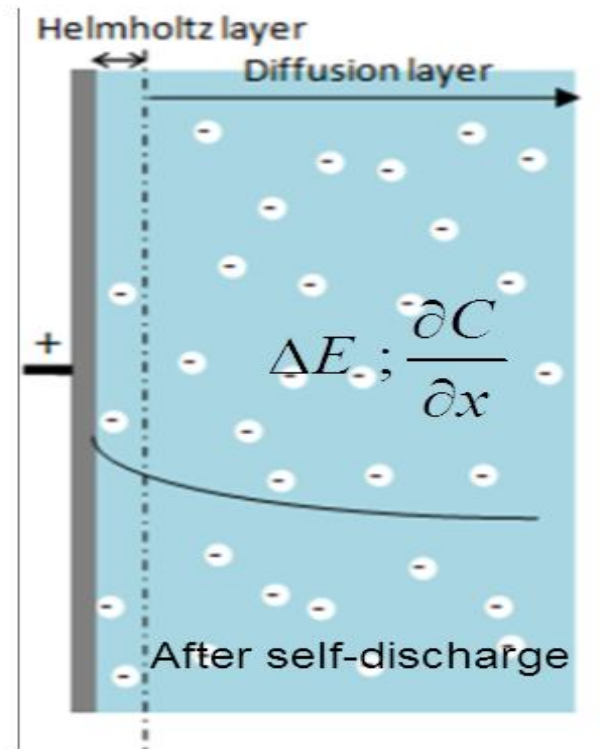
OVERVIEW



(a)



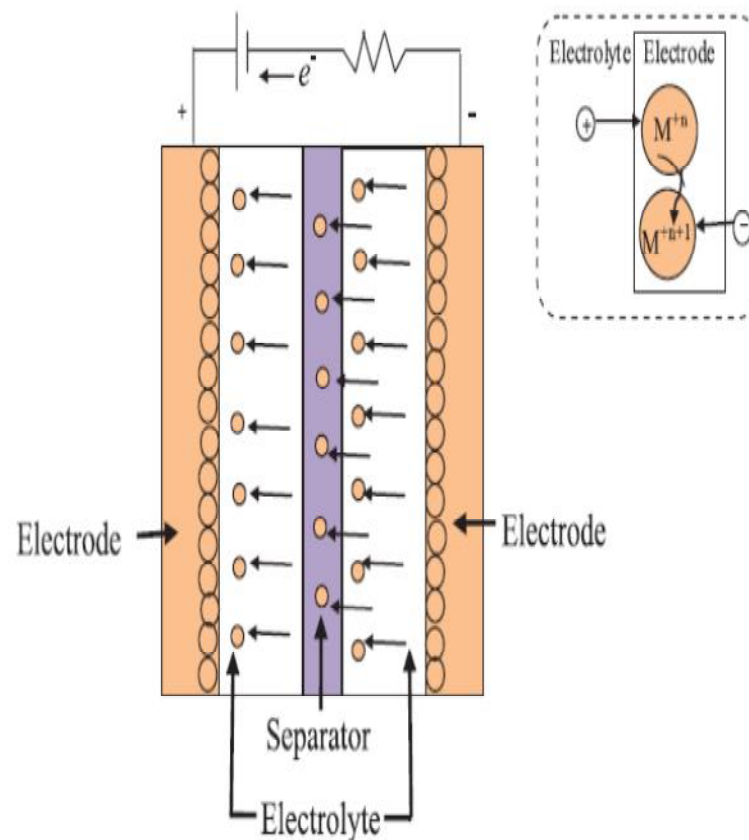
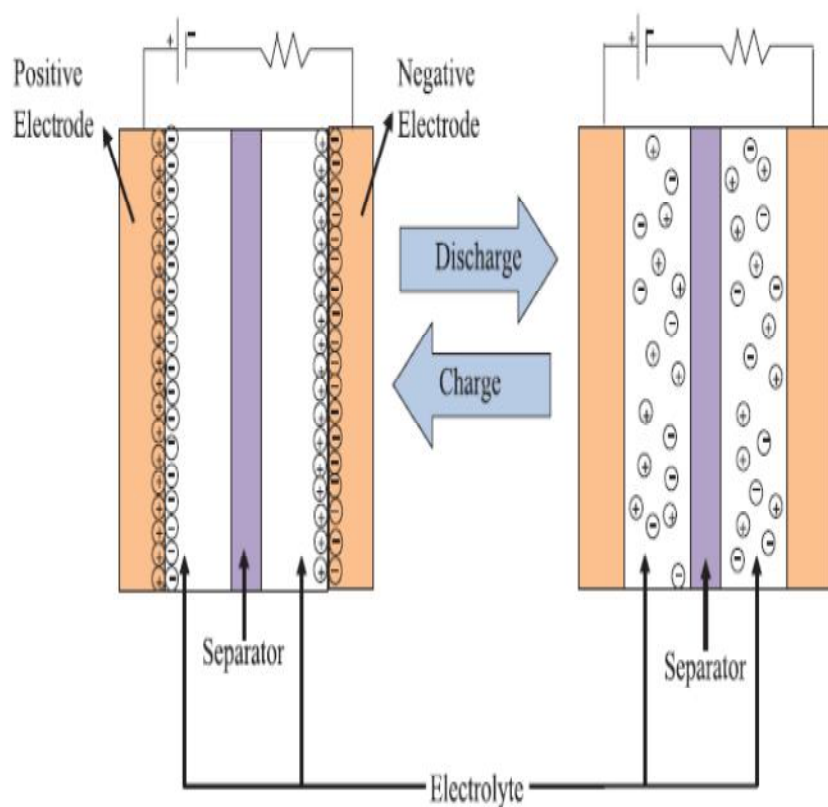
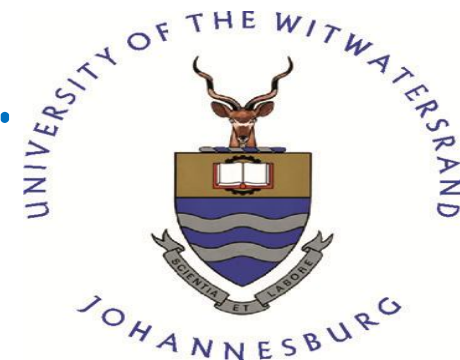
(b)



Schematic illustration on the self-discharge process (Note: ΔE -potential field; $\frac{\partial C}{\partial x}$ -concentration gradient of ions)



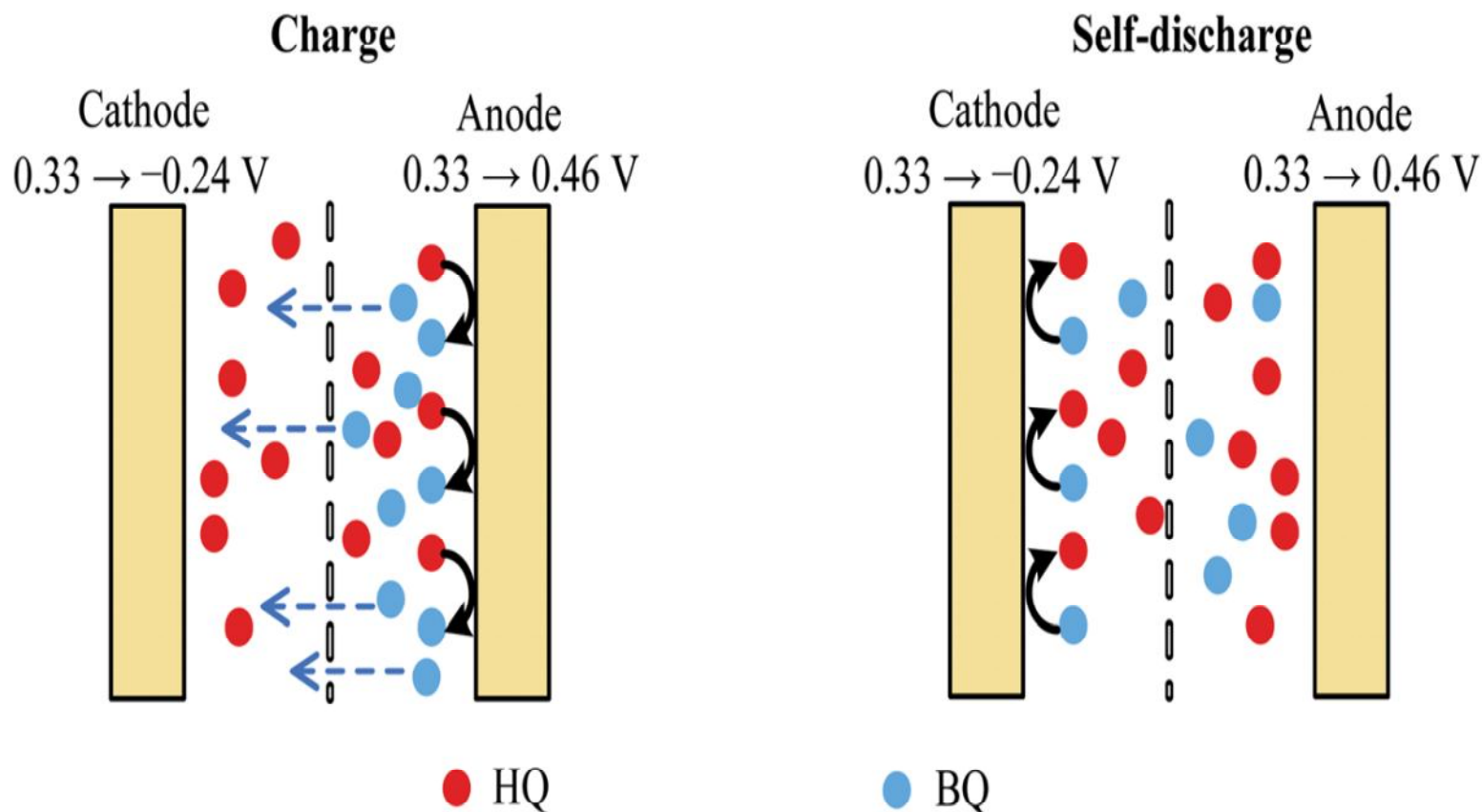
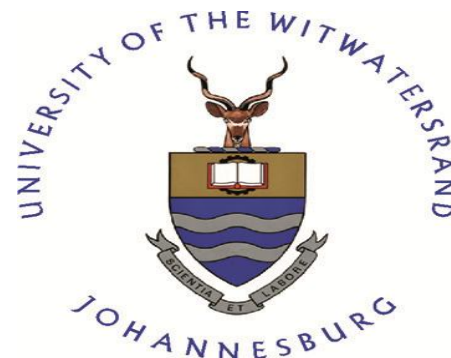
OVERVIEW CONT.



Mechanism of charge/discharge process for symmetric EDLC and energy storage mechanism for pseudocapacitor

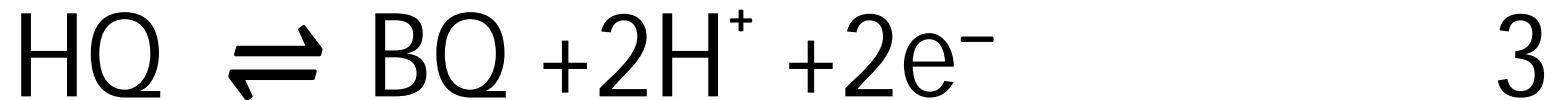
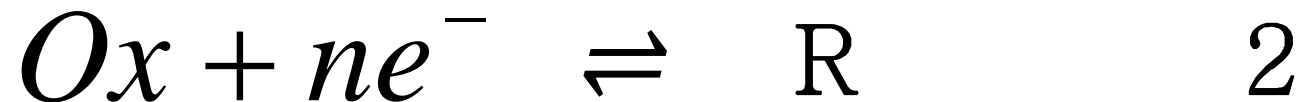
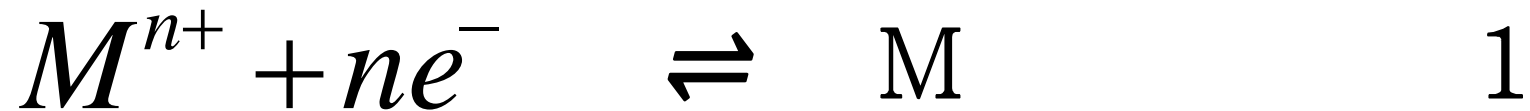


OVERVIEW CONT.



Schematic illustration of the mechanism of charge and self-discharge of active electrolyte improved supercapacitors, AEESCs

SELF-DISCHARGE MECHANISMS



Where Ox = oxidised species

R = reduced species

M = metals such as iron, manganese and titanium

n = number of electrons transferred per molecule of reactant

The Model Equations Self-discharge term

$$\frac{\partial \varphi_{ne}(x,t)}{\partial t} = \beta^2 \frac{\partial^2 \varphi_{ne}(x,t)}{\partial x^2} + \frac{J_{VR}(x,t)}{C_V} \quad 4$$

$$\beta^2 = \frac{\alpha_1 \alpha_2}{C_V(\alpha_2 + \alpha_1)} \quad 5$$

$$J_{VR} = \frac{eZN}{w_{sp} \left(\frac{s_+ + s_-}{s_+ s_-} + \frac{D_+ + D_-}{D_+ D_-} \right)} \quad 6$$

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

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

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

and the initial condition is as follows:

$$\varphi_{ne}(x,0) = \varphi^{0+} \quad 9$$

Solution for Model Equations

$$\begin{aligned} \varphi_{ne}(x, t) = \varphi^{eff} \pm \frac{J_0}{w_{ne}C_V} \left\{ t + C_V \left[\frac{(\alpha_2 + \alpha_1)}{2\alpha_1\alpha_2} x^2 - \frac{w_{ne}x}{\alpha_1} - \frac{2w^2}{\pi^2} \right. \right. \\ \left. \left. \sum_{n=1}^{\infty} \left(\frac{1}{\alpha_1} + \frac{(-1)^n}{\alpha_2} \right) \frac{e^{-\frac{\beta^2 n^2 \pi^2 t}{w^2}}}{n^2} \cos\left(\frac{n\pi x}{w}\right) \right] \right\} + \frac{J_{VR}t}{C_V} + \frac{2w^2 J_{VR}}{\pi^3} \\ \sum_{n=1}^{\infty} \frac{(-1)^n (\alpha_2 + \alpha_1)}{\alpha_1 \alpha_2} \left(\frac{1 - e^{-\frac{\beta^2 n^2 \pi^2}{w^2}(t-t_0)}}{n^3} \right) \cos\left(\frac{n\pi x}{w}\right) \end{aligned} \quad 10$$

$$\varphi^{eff} = \varphi^{0+} \pm \frac{J_0 w_{ne} (2\alpha_2 - \alpha_1)}{6\alpha_1 \alpha_2} \quad 11$$

$$\begin{aligned} \varphi_{ne}(x, t) = \varphi^{eff} \pm \frac{J_0}{w_{ne}C_V} \left\{ t + C_V \left[\frac{(\alpha_2 + \alpha_1)}{2\alpha_1\alpha_2} x^2 - \frac{w_{ne}x}{\alpha_1} - \frac{2w^2}{\pi^2} \right. \right. \\ \left. \left. \sum_{n=1}^{\infty} \left(\frac{1}{\alpha_1} + \frac{(-1)^n}{\alpha_2} \right) \frac{e^{-\frac{\beta^2 n^2 \pi^2 t}{w^2}}}{n^2} \cos\left(\frac{n\pi x}{w}\right) \right] \right\} \end{aligned} \quad 12$$

RESULTS AND DISCUSSIONS

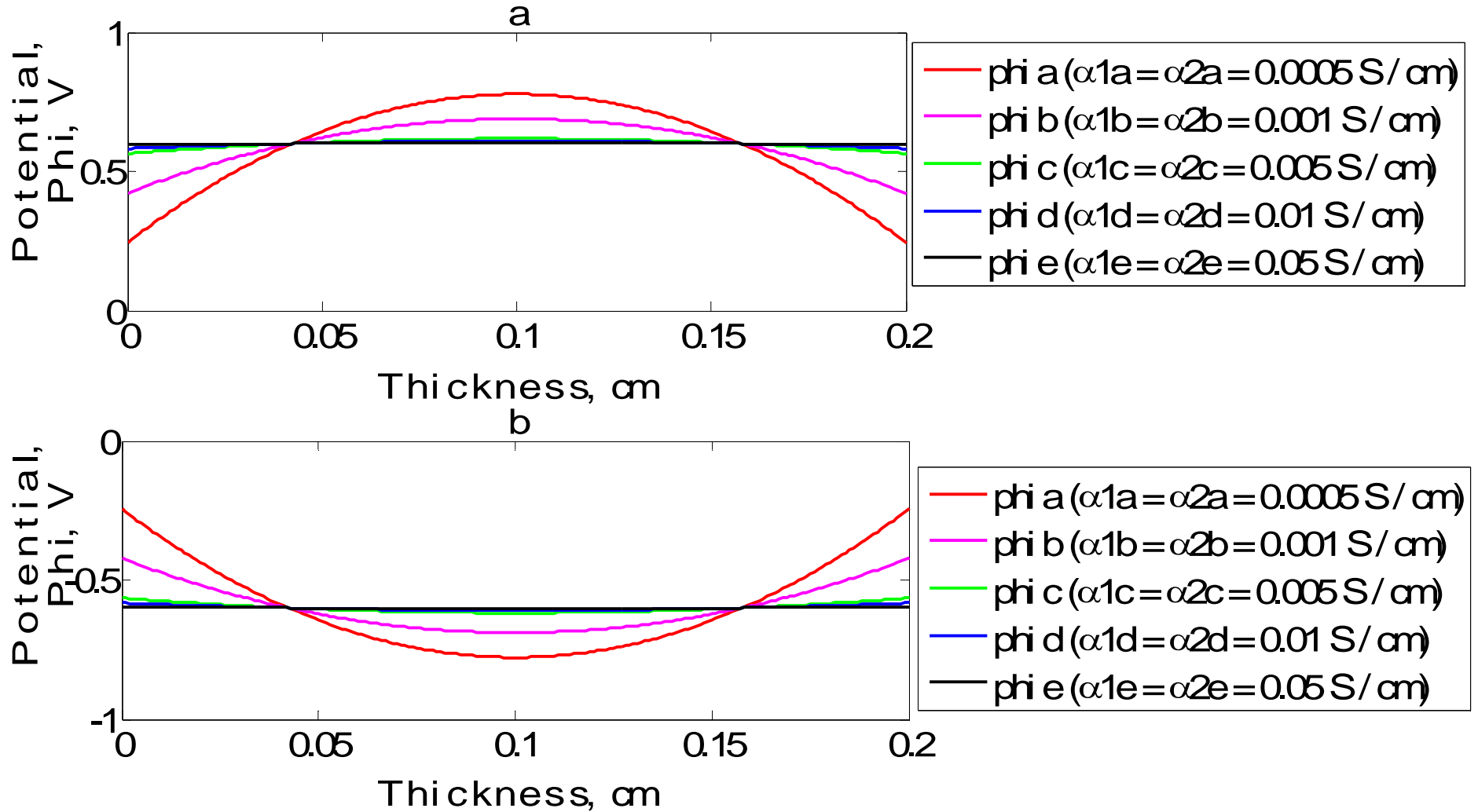


Figure 1: Potential profile for the electrode as a function of position before (a) charge process for both with and without self-discharge effect and (b) discharge process for both with and without self-discharge effect by constant current with different values of α_1 and α_2

RESULTS AND DISCUSSIONS CONT.

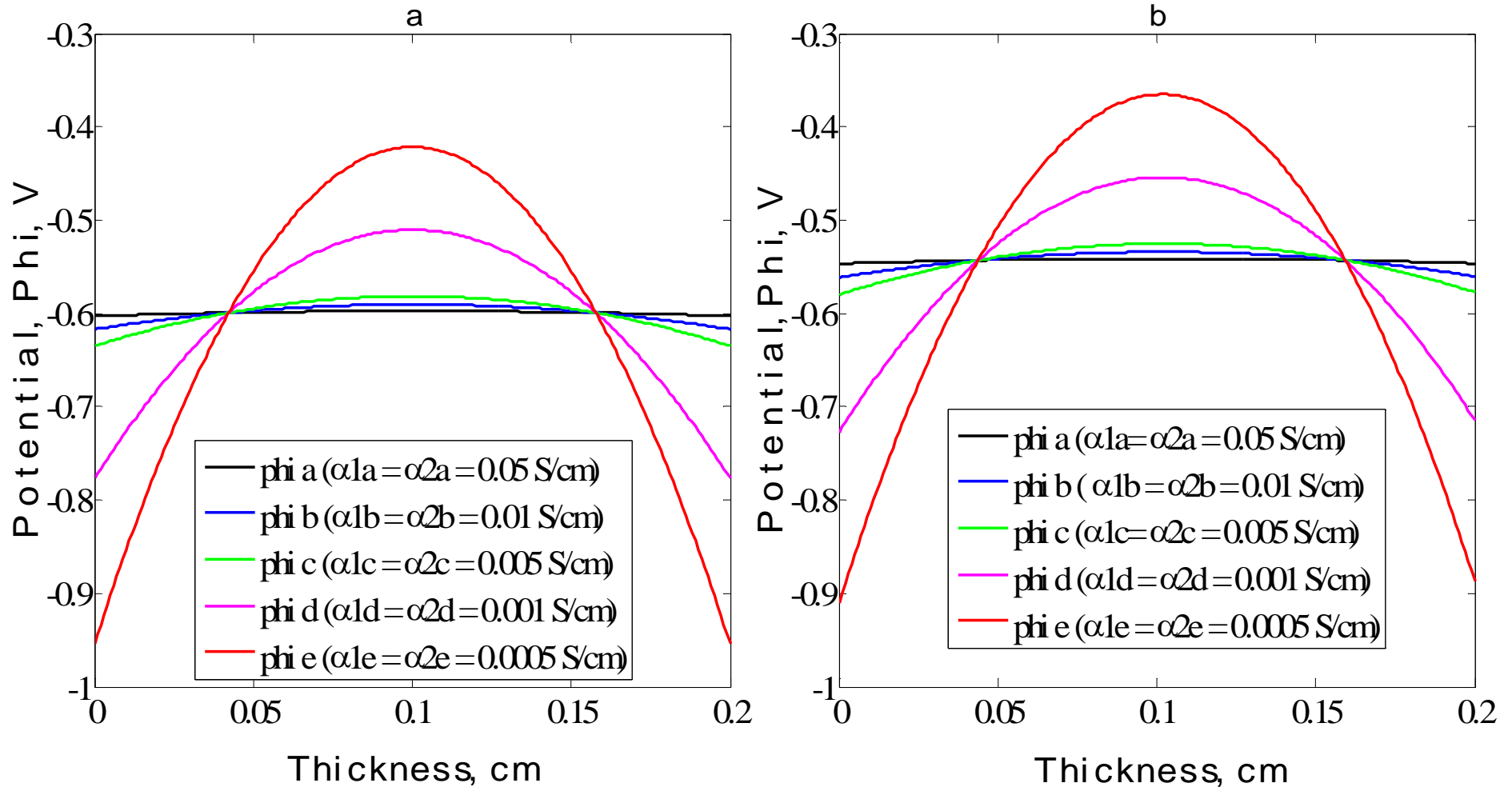


Figure 2: Potential profile for the electrode as a function of position after (a) charge process without self-discharge effect and (b) charge process with self-discharge effect by constant current with different values of α_1 and α_2

RESULTS AND DISCUSSIONS CONT.

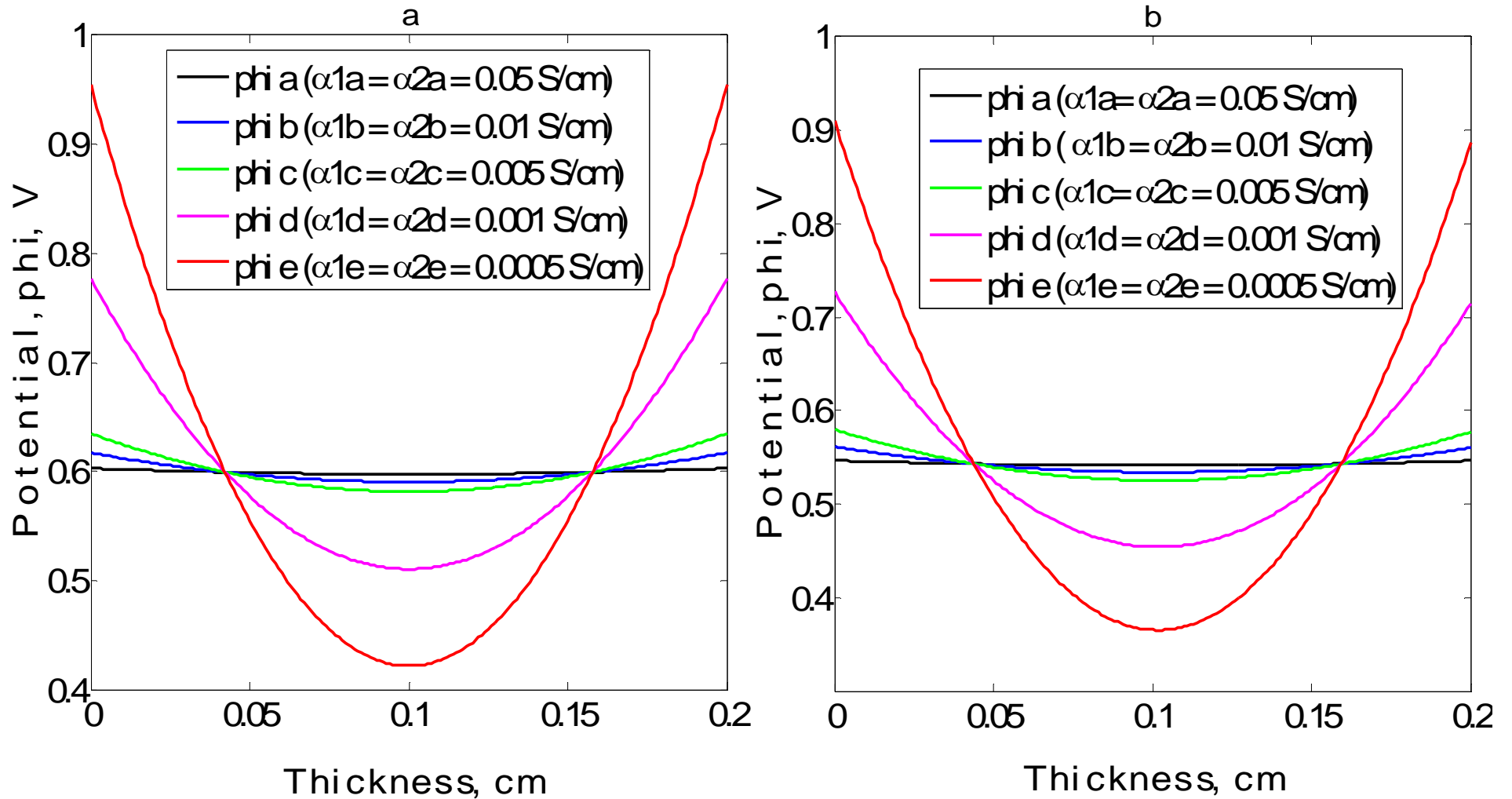


Figure 3: Potential profile for electrode as a function of position after (a) discharge process without self-discharge effect and (b) discharge process with self-discharge effect by constant current with different values of α_1 and α_2

RESULTS AND DISCUSSIONS CONT.

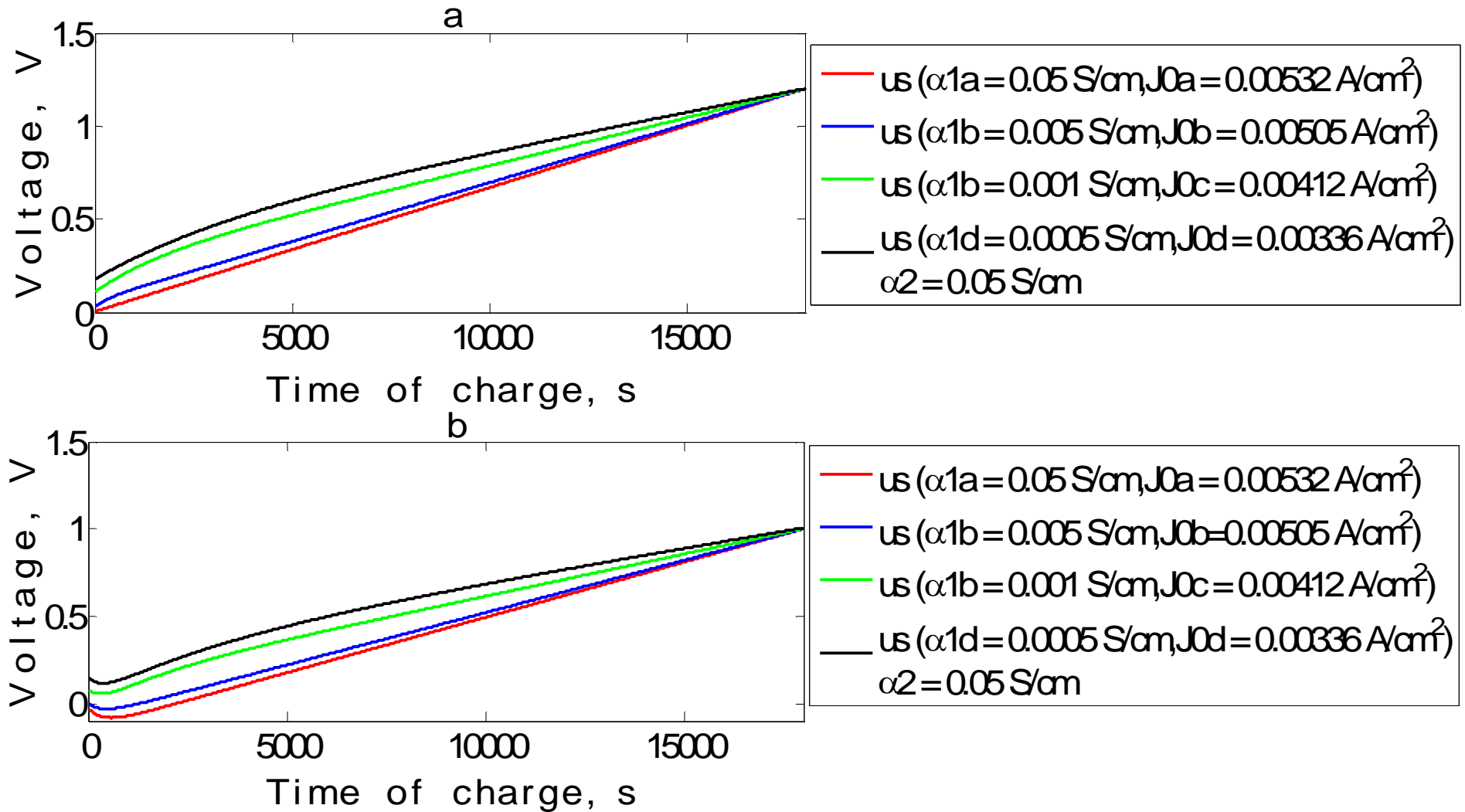


Figure 4: Electrochemical capacitor emf dependence on time during (a) charging without self-discharge and (b) charging with self-discharge effect and with different parameters charging from emf = 0.0 V to emf = 1.2V for 5 hours charging period

RESULTS AND DISCUSSION CONT.

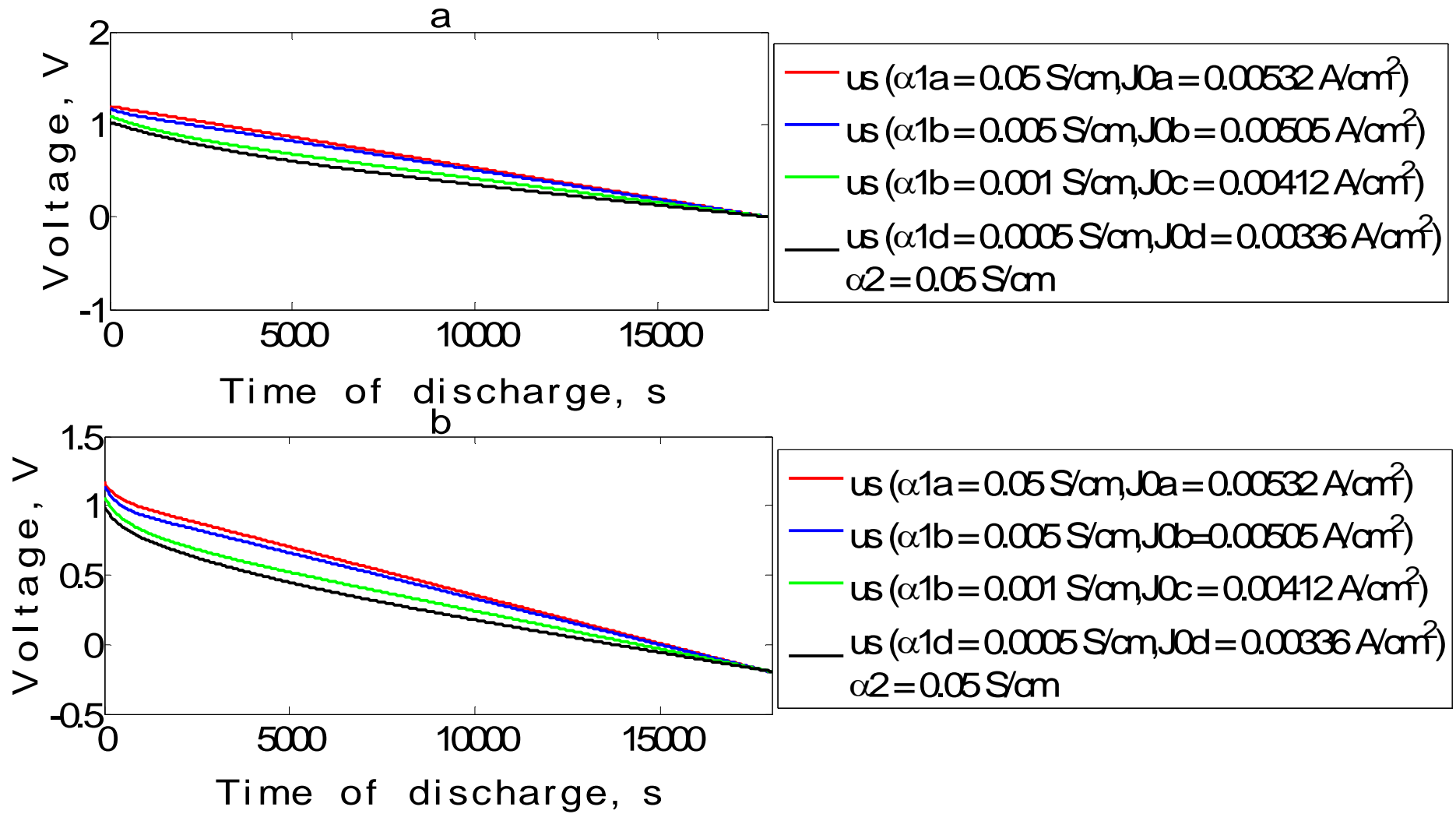


Figure 5: Electrochemical capacitor emf dependence on time during (a) discharging without self-discharge and (b) discharging with different parameters discharging from emf = 1.2V to emf = 0.0 V with self-discharge effect for 5 hours discharging period

RESULTS AND DISCUSSION CONT.

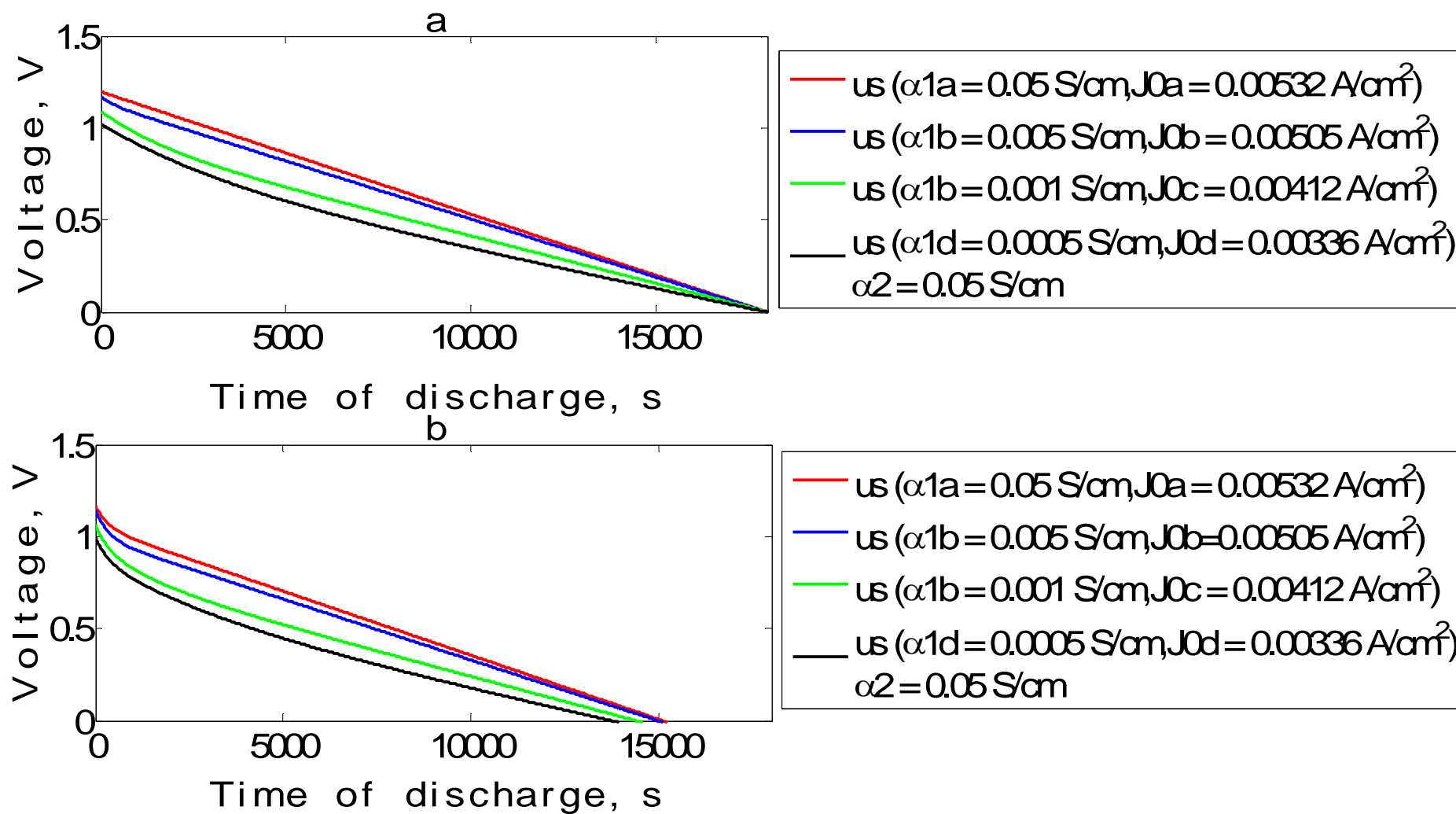


Figure 6: Electrochemical capacitor emf dependence on time during (a) discharging without self-discharge effect for 5 hours discharging period and (b) discharging with different parameters discharging from emf = 1.2V to emf = 0.0 V with self-discharge effect.

RESULTS AND DISCUSSION CONT.

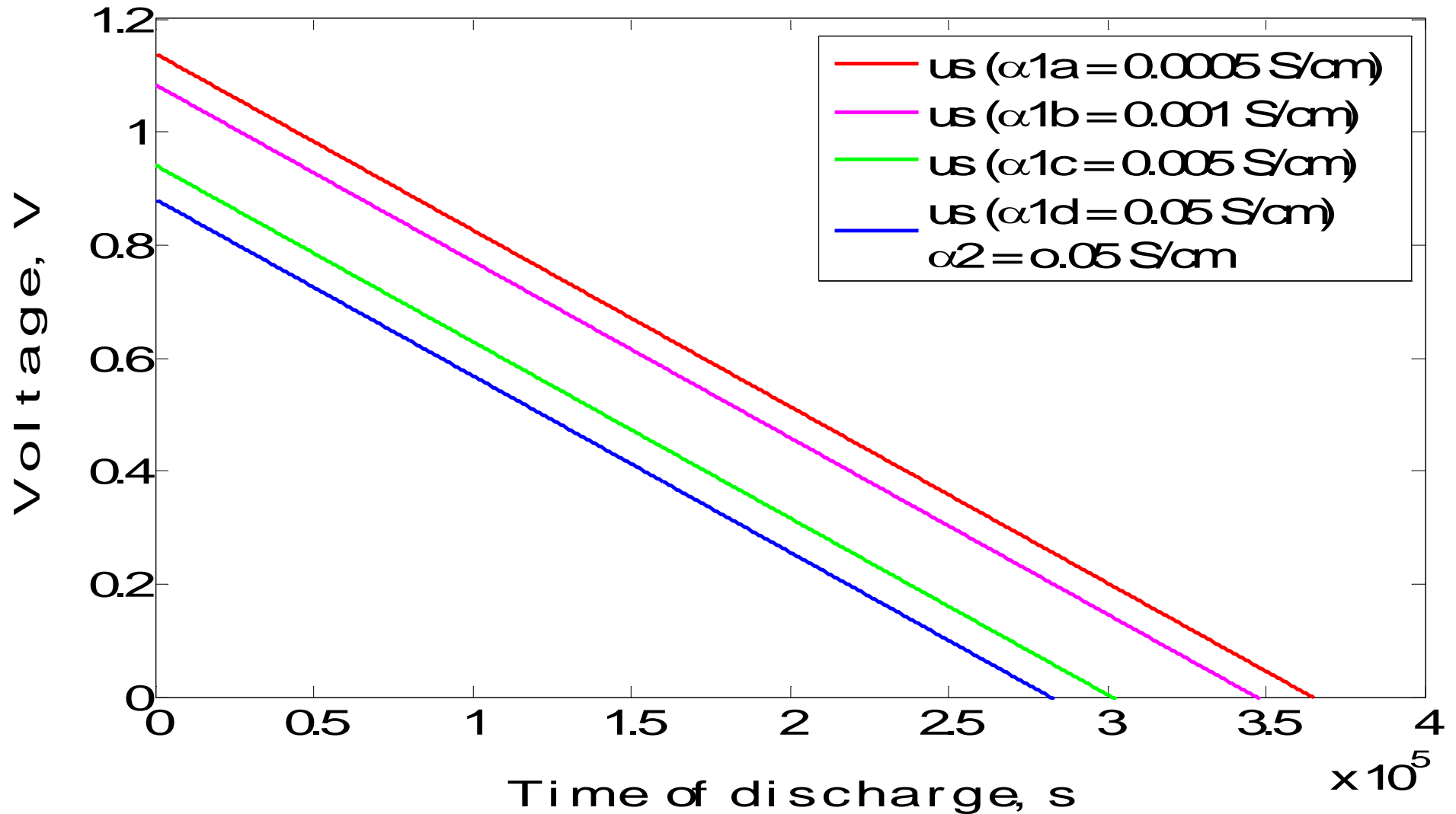


Figure 7: Dependence of Voltage on time of storage of the symmetric EDLC with self-discharge and different electrodes effective conductivity for Case 1 ($N=10^{20} \text{ cm}^{-3}$, $w_{sp}=0.05 \text{ cm}$, $J_{VR}(x,t)=0.00125 \text{ A/cm}^3$).

RESULTS AND DISCUSSION CONT.

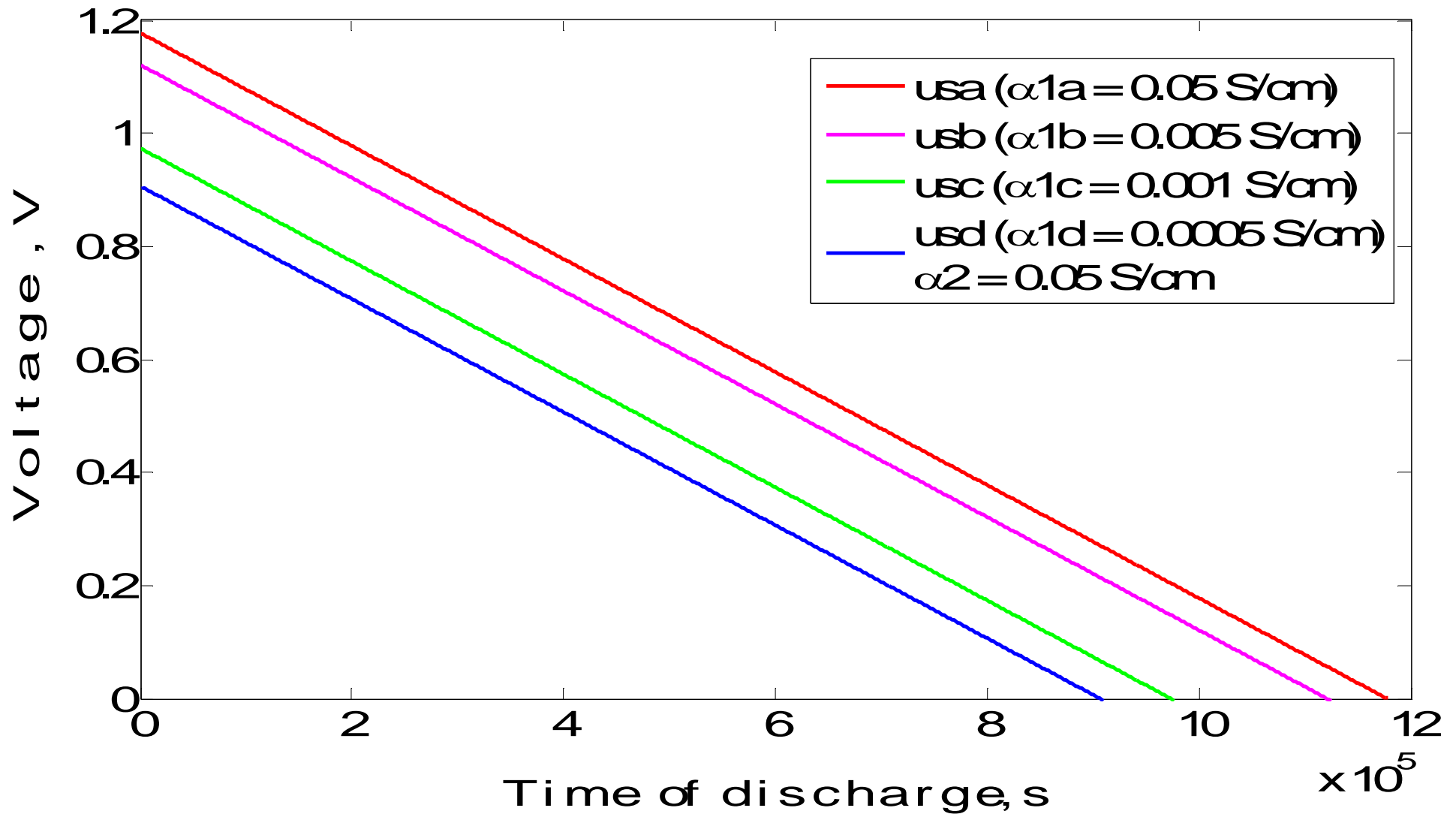


Figure 8: Dependence of Voltage on time of storage of the symmetric EDLC with self-discharge and different electrodes effective conductivity for Case 2 ($N=10^{19} \text{ cm}^{-3}$, $w_{sp} = 0.1 \text{ cm}$, $J_{VR}(x,t) = 0.0004 \text{ A/cm}^3$).

RESULTS AND DISCUSSION CONT.

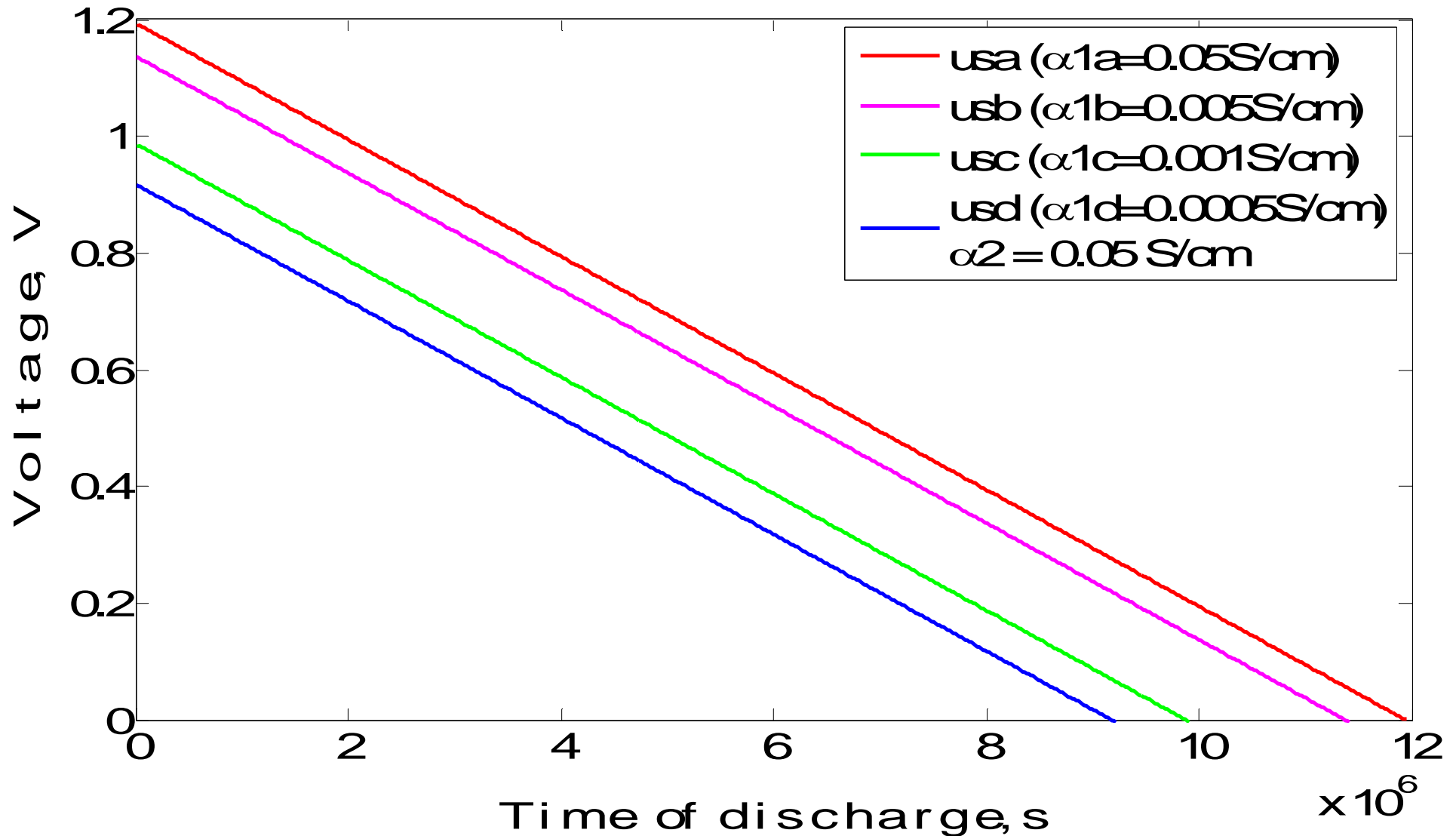


Figure 9: Dependence of Voltage on time of storage of the symmetric EDLC with self-discharge and different electrodes effective conductivity for Case 3 ($N=10^{18} \text{ cm}^{-3}$, $w_{sp}=0.1 \text{ cm}$, $J_{VR}(x,t)=0.00004 \text{ A/cm}^3$).

RESULTS AND DISCUSSION CONT.

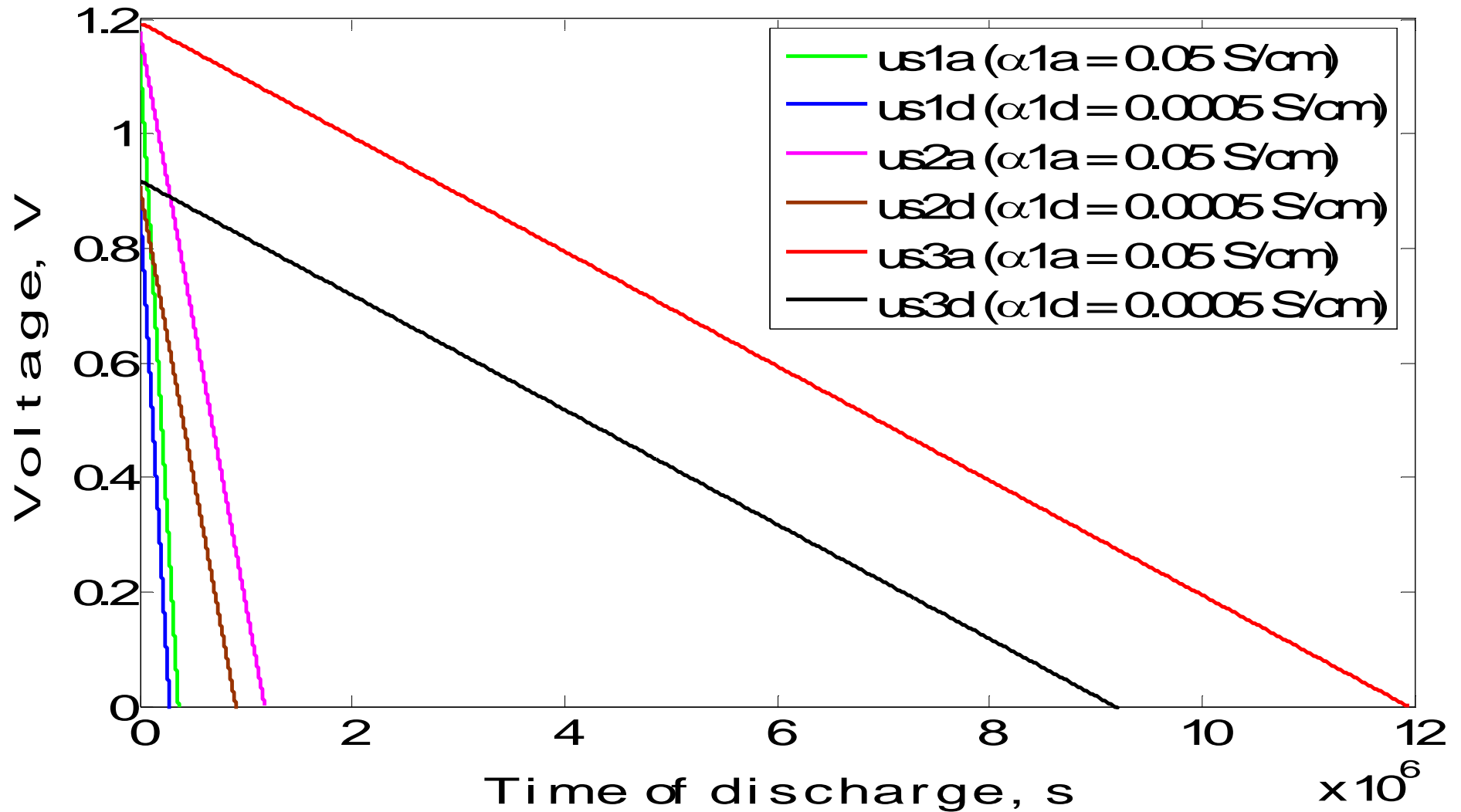


Figure 10: Dependence of Voltage on time of storage of the symmetric EDLC with self-discharge and different electrodes effective conductivity for Cases 1, 2, and 3.

RESULTS AND DISCUSSION CONT.

- Storable energy for device without self-discharge is 101.2 Wh and 96.50 Wh for with self-discharge.
- Deliverable energy for device without self-discharge is 100.1 Wh and 82.10 Wh for with self-discharge.
- Total energy loss for device without self-discharge is 17.21 Wh and 26.98 Wh for with self-discharge.
- Total energy lost due to self-discharge is 9.73 Wh.
- Shuttle ions enters the anode crystal lattice and worsen the capacity parameters, cycle life of anode and the device in general
- Energy efficiency of the first charge-discharge cycle for device without self-discharge is 84.241 % and 64.62 % for with self-discharge.
- Energy efficiency of the second charge-discharge cycle for device without self-discharge is 84.244 % and 64.63 % for with self-discharge.

Table 1: EDLCs Parameters during charge and discharge

S/N	Parameter	Unit	$\alpha_2 = 0.05 \text{ S/cm}$ and $\alpha_1 = 0.0005 \text{ S/cm}$			
			No Self-discharge	Case 1, $J_{VR} = 0.00125 \text{ A/cm}^3$	Case 2, $J_{VR} = 0.0004 \text{ A/cm}^3$	Case 3, $J_{VR} = 0.00004 \text{ A/cm}^3$
1	E_{Sch}	Wh	87.240	82.210	85.820	87.130
2	$E_{selfdis}$	Wh	0.0000	13.84	4.6740	0.4740
3	$t_{selfdisrest}$	Days	0.0000	3.2680	10.504	106.28
4	EDasy	Wh/kg	32.130	33.137	32.947	32.368
5	EEDasy	Wh/kg	30.992	27.562	28.053	29.953
6	PDasy	W/kg	6.4099	6.6109	6.8747	6.8890
7	EPDasy	W/kg	6.1829	5.5960	5.8986	6.0066
8	η_{E1}	%	54.600	28.039	41.520	49.770
9	η_{E2}	%	54.620	32.386	56.640	51.250

Table 2: EDLCs Parameters during charge and discharge

S/N	Parameter	Unit	$\alpha_1 = \alpha_2 = 0.05 \text{ S/cm}$			
			No Self-discharge	Case 1, $J_{VR} = 0.00125 \text{ A/cm}^3$	Case 2, $J_{VR} = 0.0004 \text{ A/cm}^3$	Case 3, $J_{VR} = 0.00004 \text{ A/cm}^3$
1	E_{Sch}	Wh	101.20	96.500	98.220	100.90
2	$E_{selfdis}$	Wh	0.0000	9.7330	3.0330	0.3103
3	$t_{selfdisrest}$	Days	0.0000	4.2235	13.640	138.27
4	EDasy	Wh/kg	38.810	40.345	39.490	38.978
5	EEDasy	Wh/kg	35.957	32.582	33.895	35.282
6	PDasy	W/kg	7.7425	6.9980	7.2004	7.6989
7	EPDasy	W/kg	7.1734	6.2933	6.4641	6.9393
8	η_{E1}	%	84.241	64.620	78.780	83.710
9	η_{E2}	%	84.244	64.630	78.790	84.210

CONCLUSIONS

- The model is generic and applies to any symmetric EDLC via applicable self-discharge mechanism(s);
- Diffusion coefficient, impurity concentrations and thickness of separator strongly influences the self-discharge;
- models with self-discharge took longer time to charge the device to designed voltage and discharges stored energy faster than those without self-discharge;
- **Shuttle ions worsen the capacity parameters, cycle life of anode and the device in general.**
- Fully charged capacitors with self-discharge and $\alpha_1 = \alpha_2 = 0.05$ S/cm on storage takes 4.2 days to be fully discharged by self-discharge for case 1;
- EDLCs charge, discharge and storage time is significantly dependent on self-discharge effect, and is great to be ignored especially in devices designed for long charge and discharge.

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Thank you for your attention

Comments
&
QUESTIONS



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