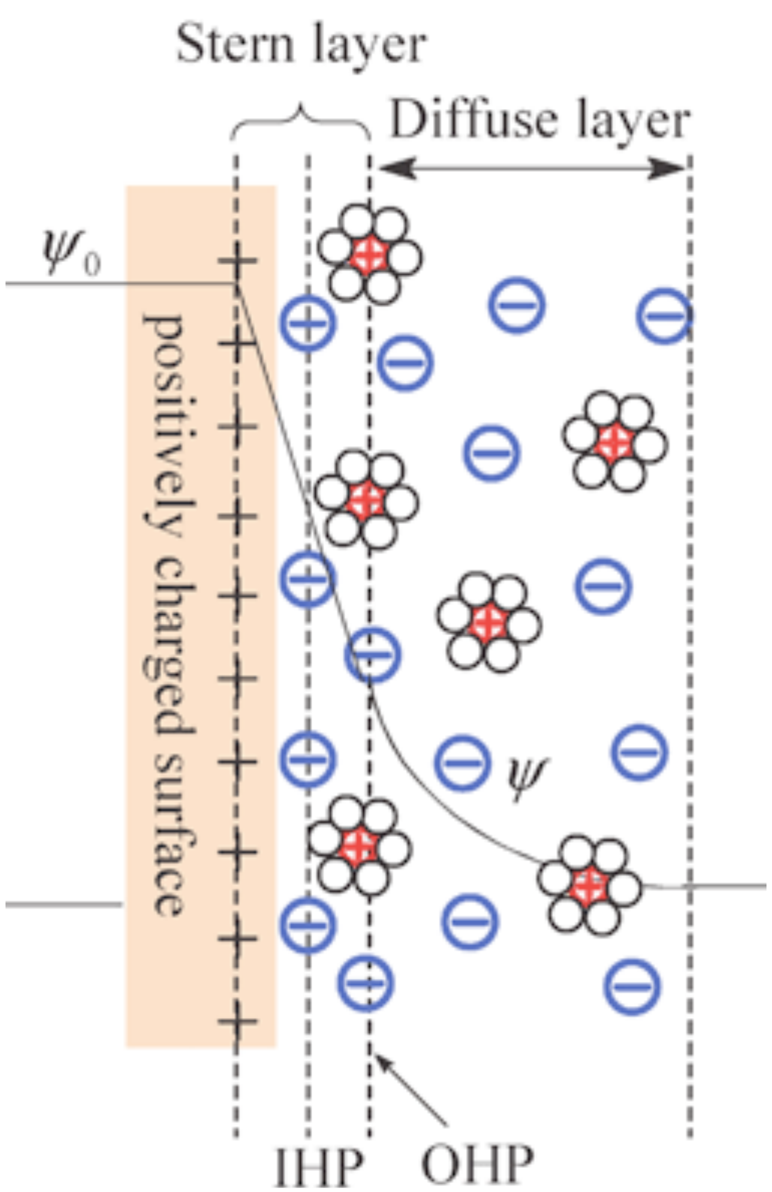
Наноматериалы в электрохимических накопителях энергии

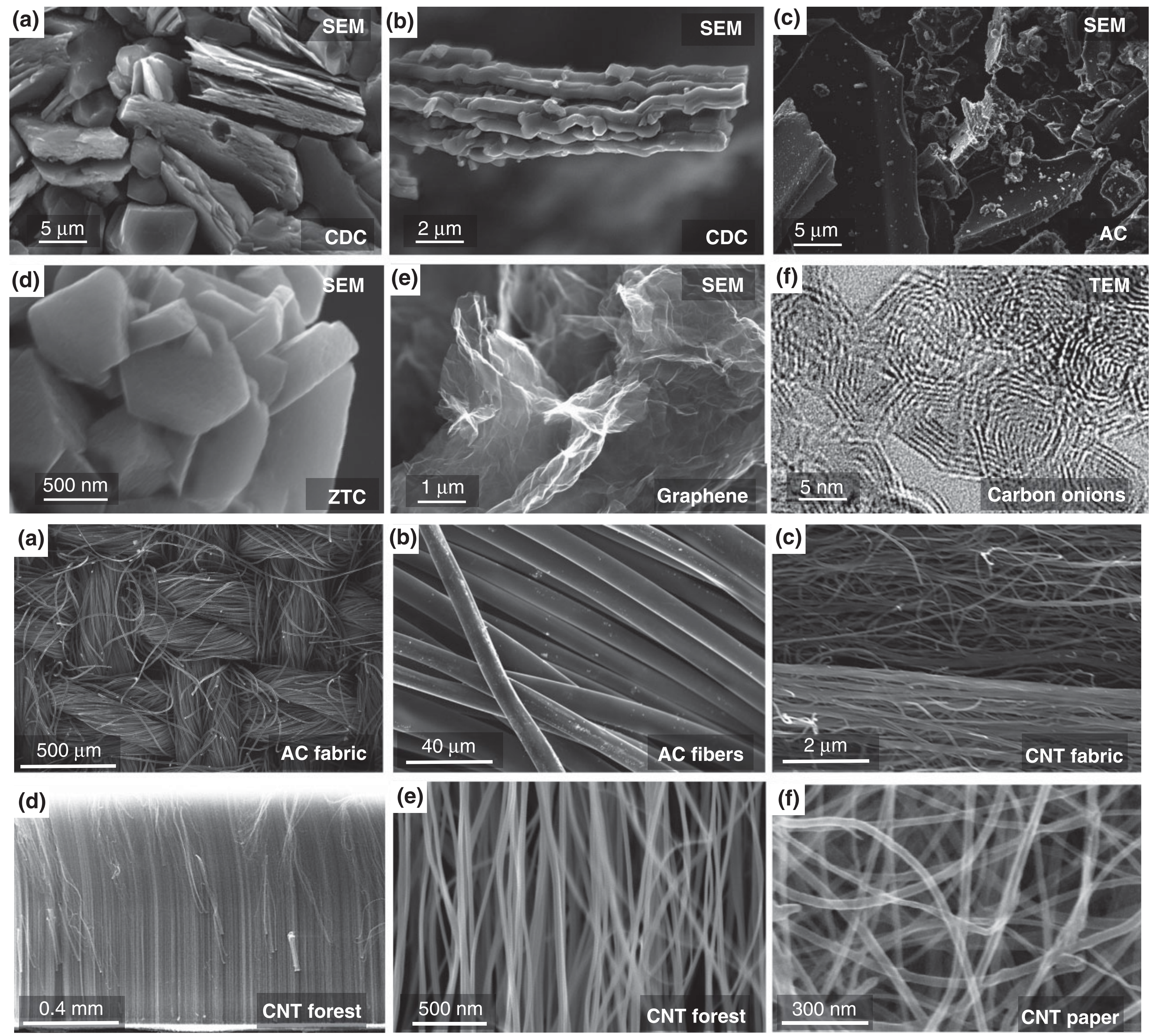
* Gartner's hype cycle

Supercapacitors



$$C = \frac{\varepsilon_r \varepsilon_0 A}{d}$$

WIREs Energy Environ 2013. doi: 10.1002/wene.102

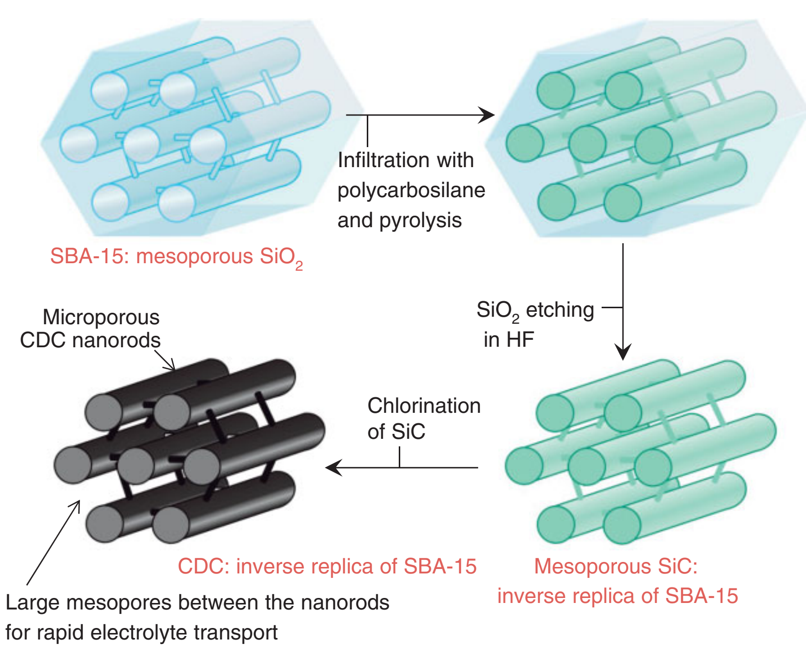


carbon source

inert atmosphere
600-900°C

CO_2, steam
250-1200°C

KOH or H_3PO_4
400-900°C



Precursor	Activation Method	BET-SSA ($m^2 g^{-1}$)	Reported Capacitance ($F g^{-1}$)/Cell Type	Electrolyte		Ref
—	Physical-H_2O	2240	240/2 symm	Organic electrolyte	1.2 M $TEABF_4$ in acetonitrile (AN)	50
—	Physical-CO_2	1050	52/2 symm		1M $TEABF_4$ in polycarbonate (PC)	51
Melamine mica	30% HNO_3 then ammonia treatment	3487	148/2 symm		1M $TEABF_4$ in PC	65
Wood sawdust	Chemical-KOH	2967	236/2 symm		1M $TEABF_4$ in AN	27
Pitch CF	Chemical-KOH	770	46/2 symm		$TEABF_4$ in PC	66
Poly(vinylidene chloride) (PVDC)	Chemical-KOH	2050	38/2 symm		1M $TEABF_4$ in PC	54
—	Chemical-KOH	2500	110/2 symm		1M $TEABF_4$ in AN	64
Polyvinyl alcohol	Chemical-KOH	2218	115/2 symm		1M Et_3MeNBF_4 in PC	49
Polyvinyl alcohol	Chemical-KOH	2218	147/2 symm		1M $LiPF_6$ in EC-DEC	49
Phenol formaldehyde resin	Chemical-KOH/$ZnCl_2$	2387	142/2 symm		1M Et_3MeNBF_4 in PC	67
Polybenzimidazol	Chemical-N_2	1220	23/2 symm		0.8M $TEABF_4$ in PC	68
Lignocellulosic materials	—	2300	95/2 symm		1.5 M $TEABF_4$ in AN	61
Lignocellulosic materials	—	2315	125/2 symm		1.7M $N(C_2H_5)_4CH_3SO_3$ in AN	62
Polyacrylonitrile (PAN)	—	1340	66/2 symm		1 M $LiPF_6$ in EC-DEC	69
PAN	—	1340	90/2 symm		1 M $TEABF_4$ in PC	70
Coconut shell	—	1692	22/2 symm		1 M $LiClO_4$ in PC	71
Pitch CF	—	1000	21/2 symm		1 M $LiClO_4$ in PC	71
Pitch CF	—	1500	24/2 symm		1 M $LiClO_4$ in PC	71
Phenol resin	—	1232	3/2 symm		1 M $LiClO_4$ in PC	71
Phenol resin	—	1542	18/2 symm		1 M $LiClO_4$ in PC	71
Pitch	—	1016	1/2 symm		1 M $LiClO_4$ in PC	71
Pitch	—	1026	2/2 symm		1 M $LiClO_4$ in PC	71
Sulfonated poly(divinylbenzene)	physical-CO_2	2420	206/3	Aqueous electrolyte	2M H_2SO_4 aq. sol.	47
Rubber wood sawdust	physical-CO_2	913	138/2 symm		1M H_2SO_4 aq. sol.	72
Poly (amide imide)	Physical-CO_2	1360	196/3		6M KOH aq. sol.	73
Pitch fiber	Physical-H_2O	880	28/2 symm		1M KCl aq. sol.	74
Coconut shell	Chemical-Melamine and urea	804	230/2 symm		1M H_2SO_4 aq. sol.	75
Melamine mica	Chemical-30% HNO_3 then ammonia treatment	86	115/2 symm		1M H_2SO_4 aq. sol.	65
Phenolic resin	Chemical- 2M HNO_3	—	60/2 symm		6M KOH aq. sol.	76
graphite	Chemical- HNO_3/H_2SO_4 (1:1)	—	1071/3		0.1M KOH aq. sol.	59
Rice husk	Chemical- H_2SO_4	—	175/3		6M KOH aq. sol.	40
Wood sawdust	Chemical-KOH	2967	143/2 symm		6M KOH aq. sol.	27
Eggshell	Chemical-KOH	221	297/3		6M KOH aq. sol.	41
polystyrene	Chemical-KOH	2350	258/3		6M KOH aq. sol.	77

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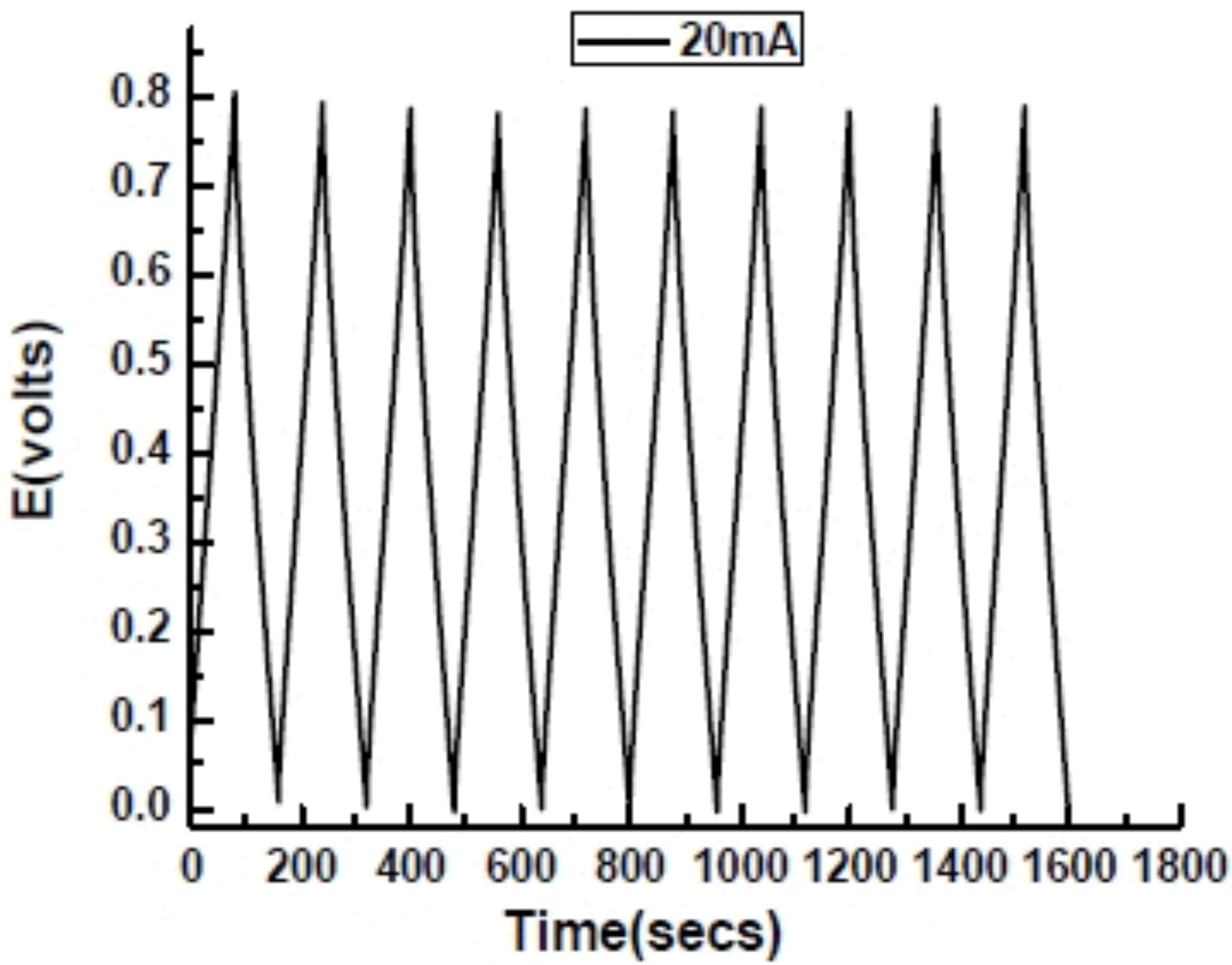
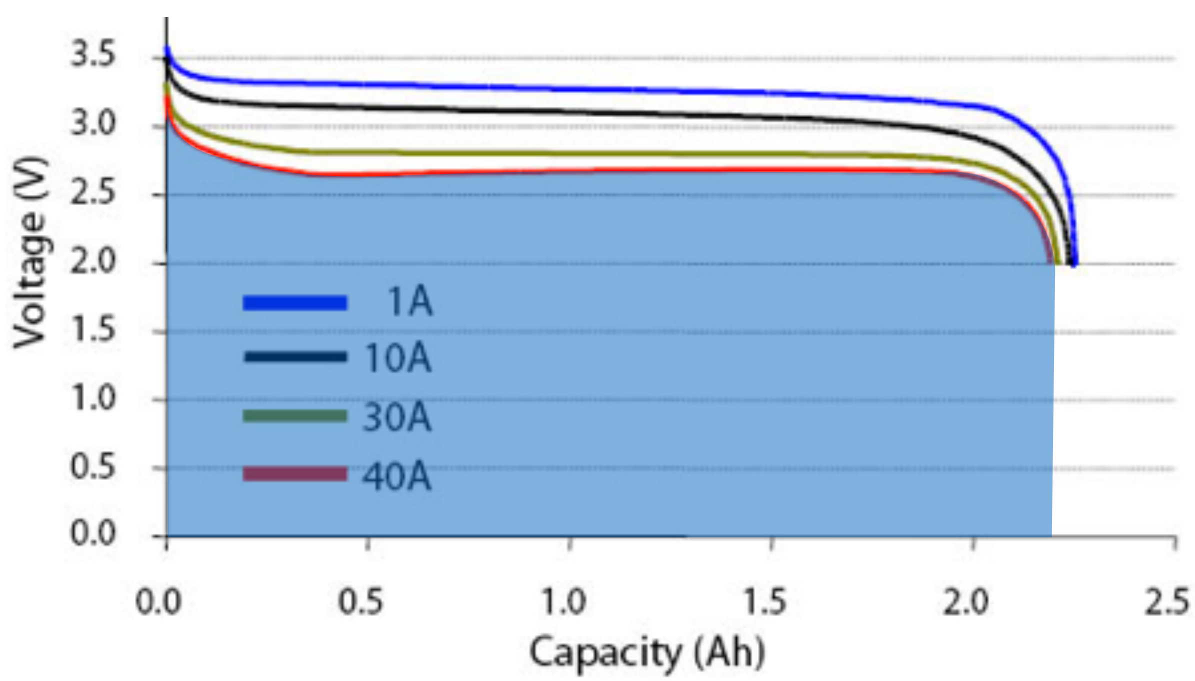
Charge/discharge of supercapacitors



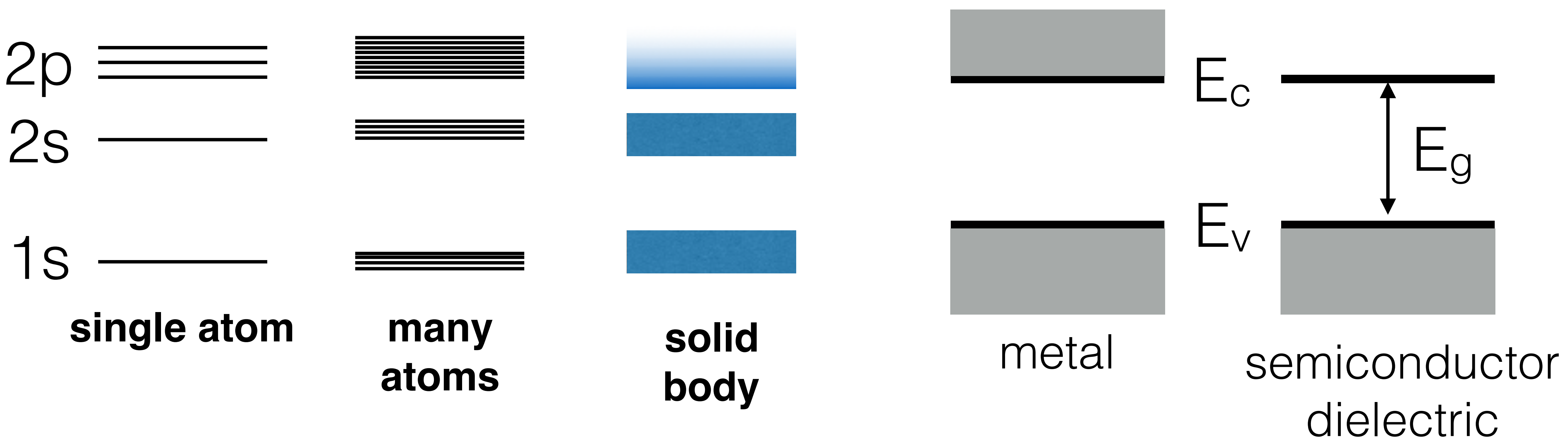
Lithium battery



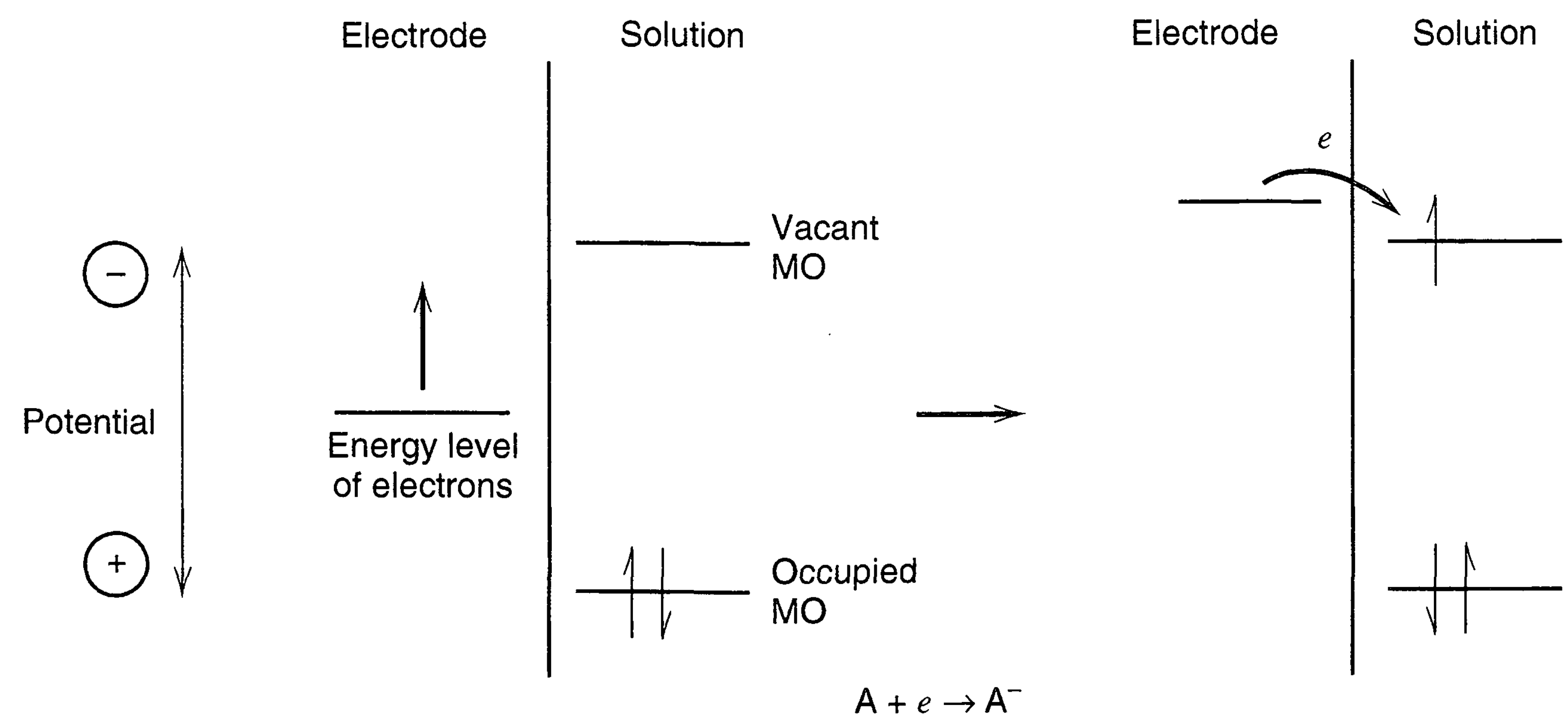
C-rate

1C - разряд/заряд за 1 час
2C – полчаса
C/2 – 2 часа

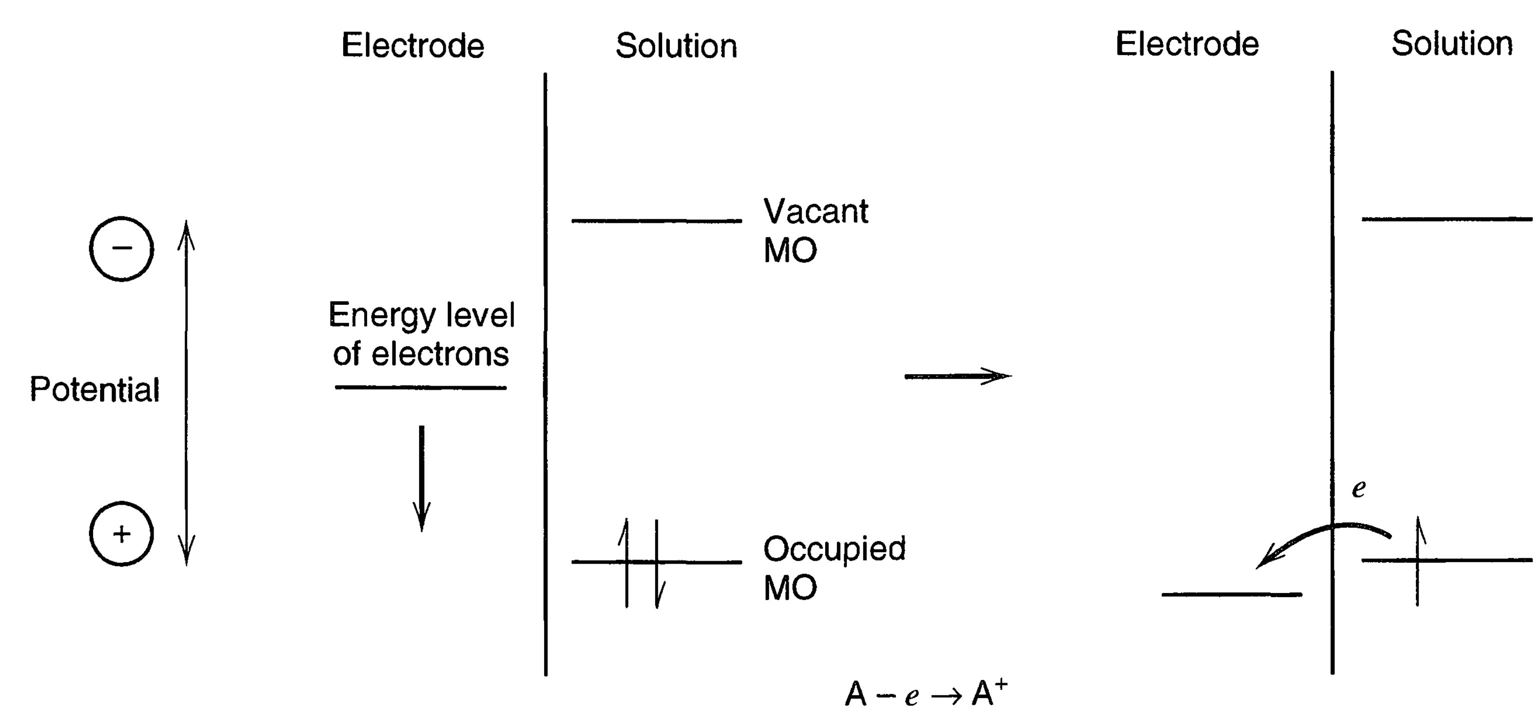
Electronic structure of a solid body

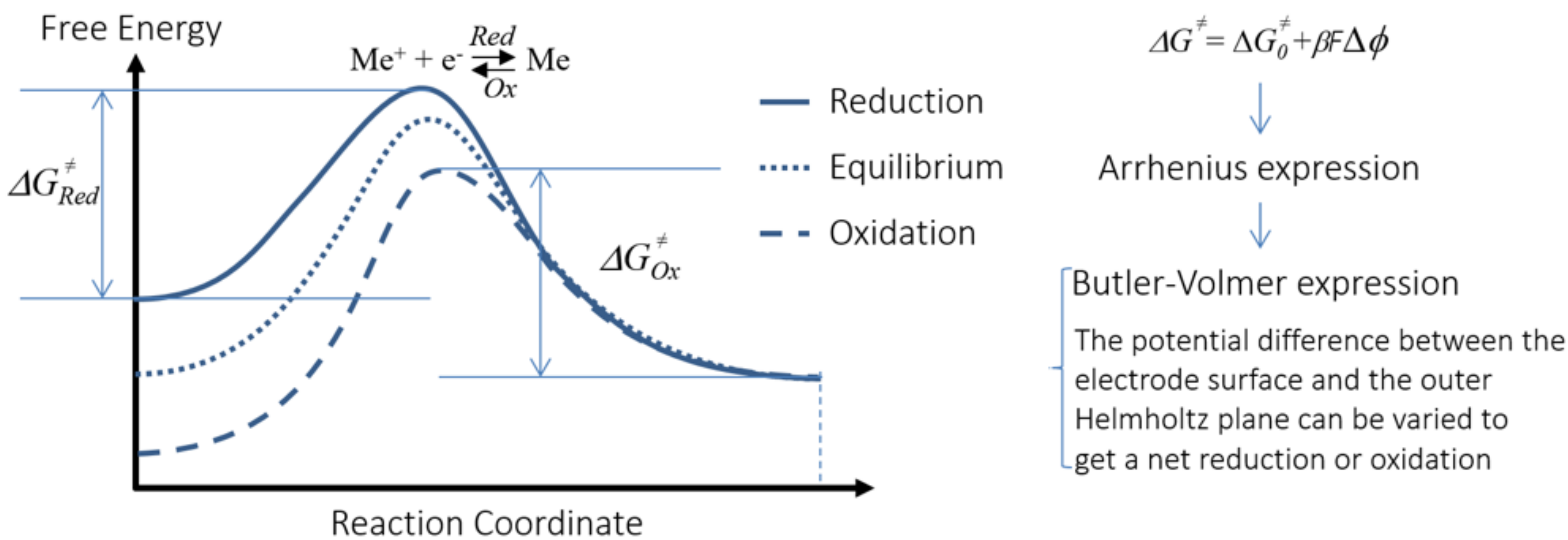


reduction

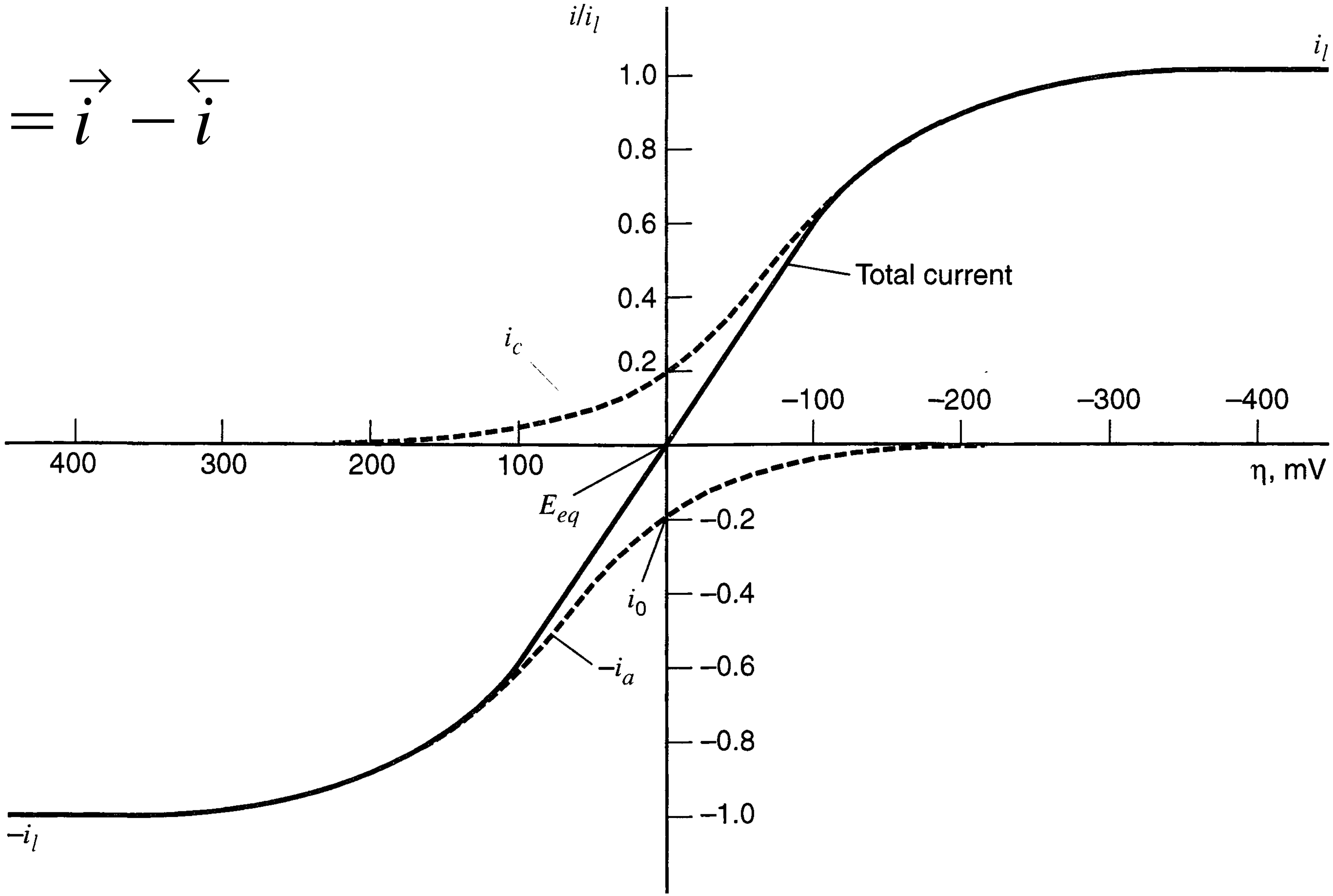


oxidation




Free Energy
$Me^+ + e^- \underset{Ox}{\overset{Red}{\rightleftharpoons}} Me$
$\Delta G^{\neq}_{Red}$
$\Delta G^{\neq}_{Ox}$
Reduction
Equilibrium
Oxidation
Reaction Coordinate
$\Delta G^{\neq} = \Delta G^{\neq}_{0} + \beta F \Delta \phi$
Arrhenius expression
Butler-Volmer expression
The potential difference between the electrode surface and the outer Helmholtz plane can be varied to get a net reduction or oxidation

$$i = \overrightarrow{i} - \overleftarrow{i}$$



$$i = i^{0}\left[\exp\left(\frac{\alpha\,\Delta E}{RT}\right) - \exp\left(\frac{-\beta\,\Delta E}{RT}\right)\right]$$

Концентрационная поляризация

ДИФФУЗИЯ

закон Фика

$$J_{d,j} = D_j \text{ grad } c_j$$

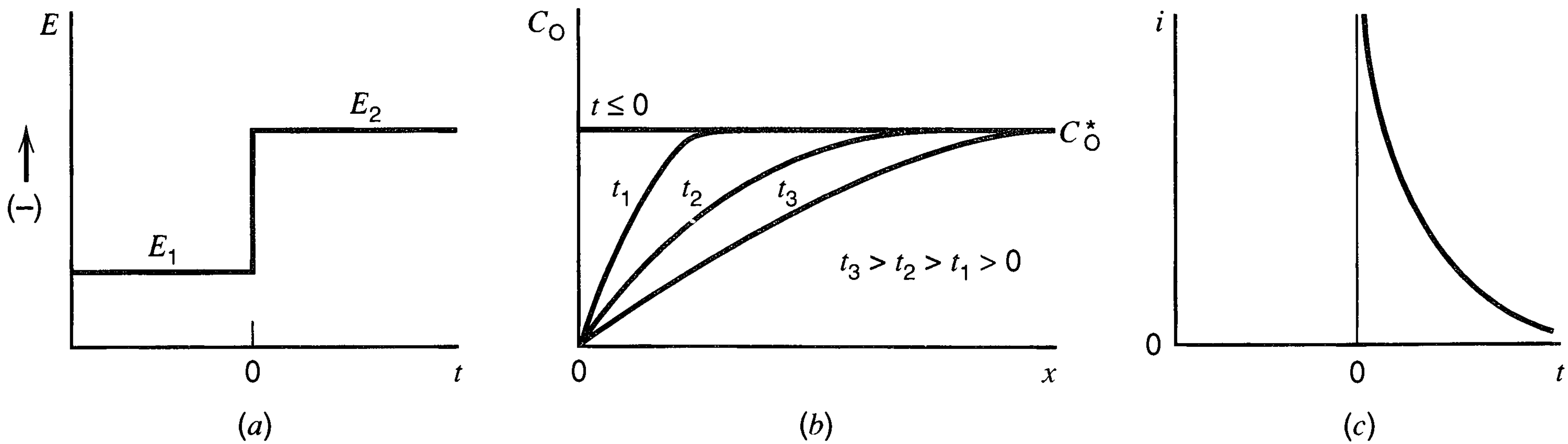
ЭЛЕКТРОМИГРАЦИЯ

уравнение Эйнштейна-Смолуховского

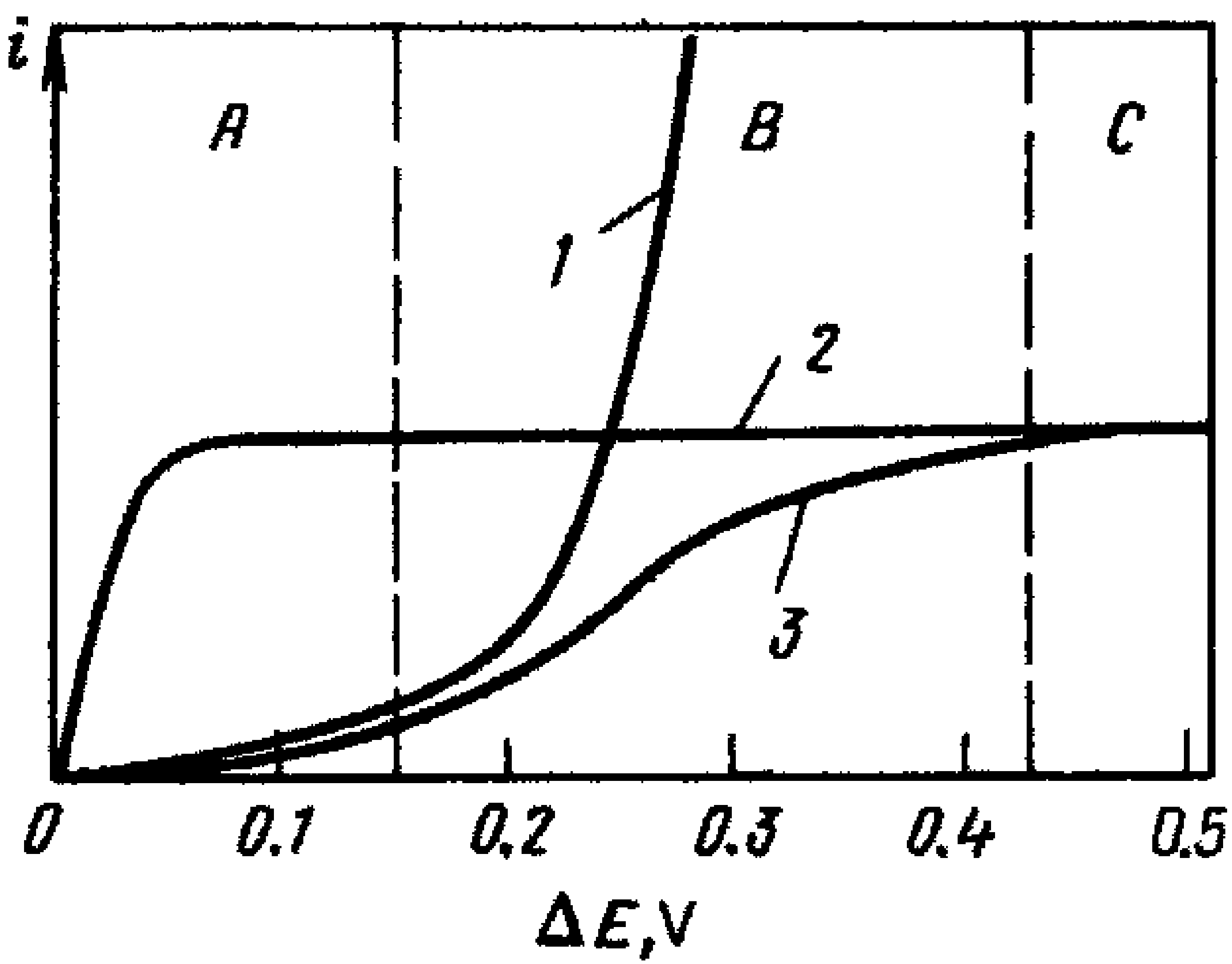
$$u_{\text{j}} = \frac{|z_{\text{j}}|FD_{\text{j}}}{RT}$$

$$u_j \equiv \frac{v_j}{\mathbf{E}}$$

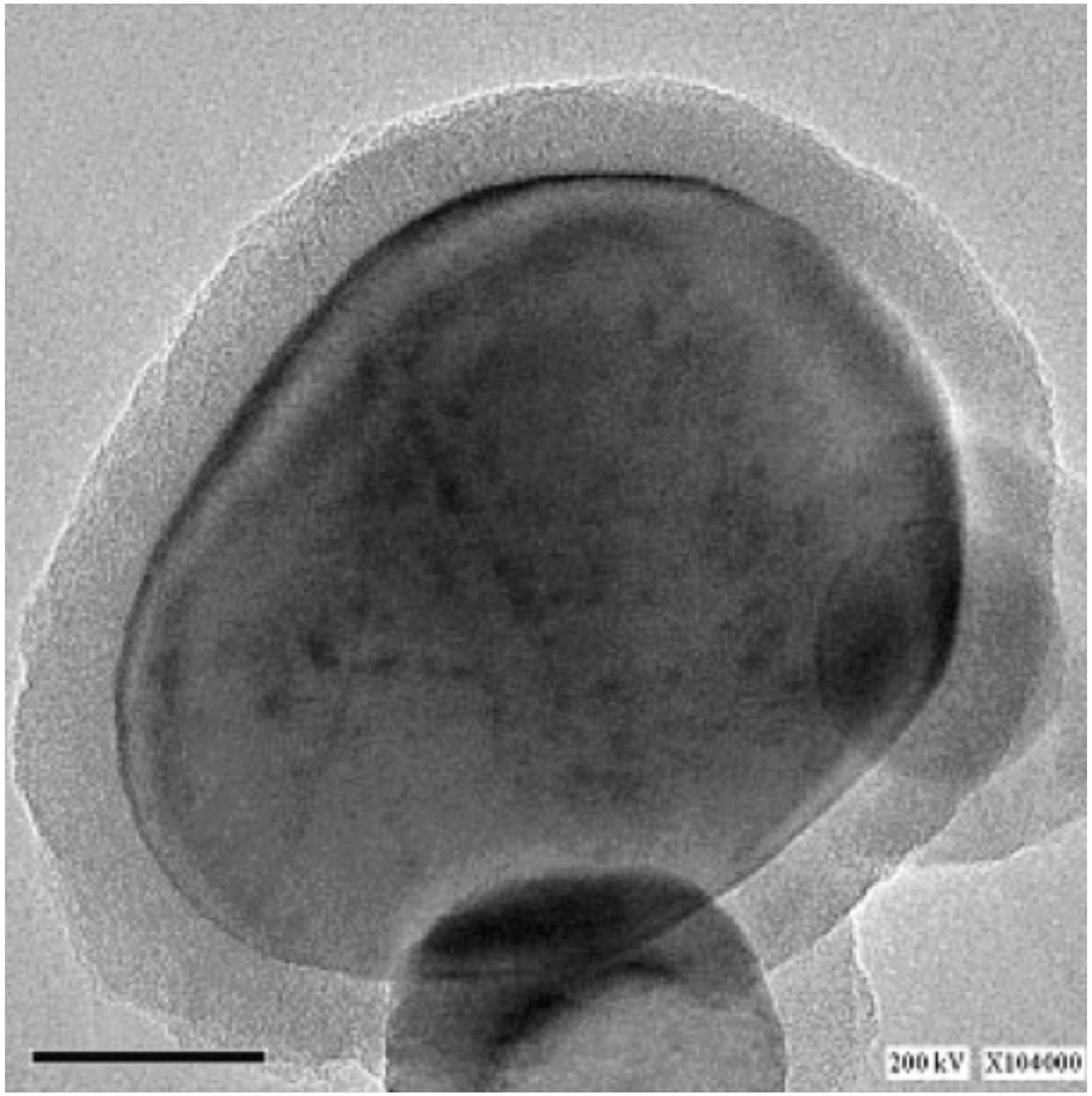
Концентрационные профили

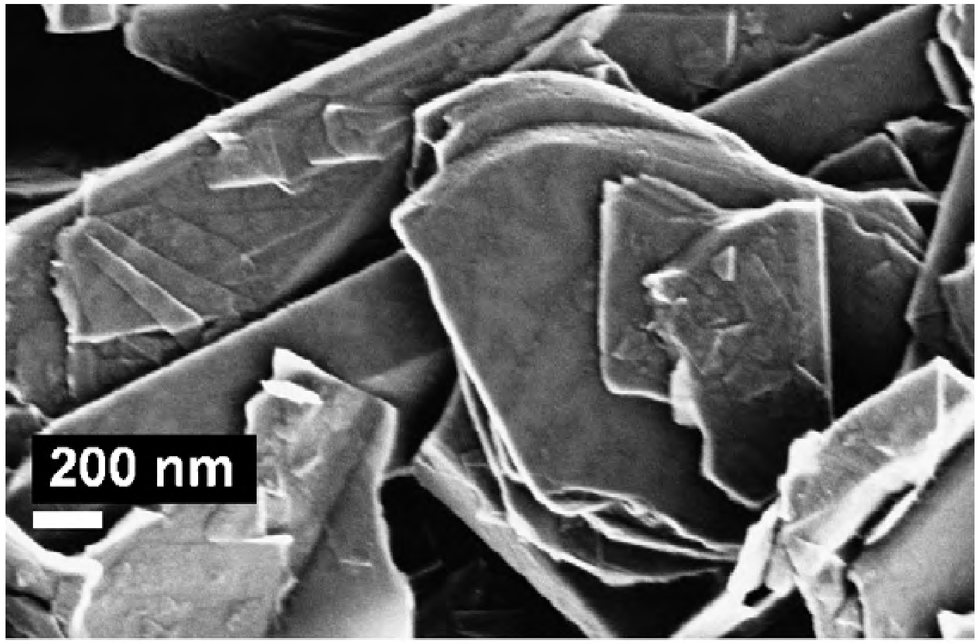


Activation + concentration polarisation

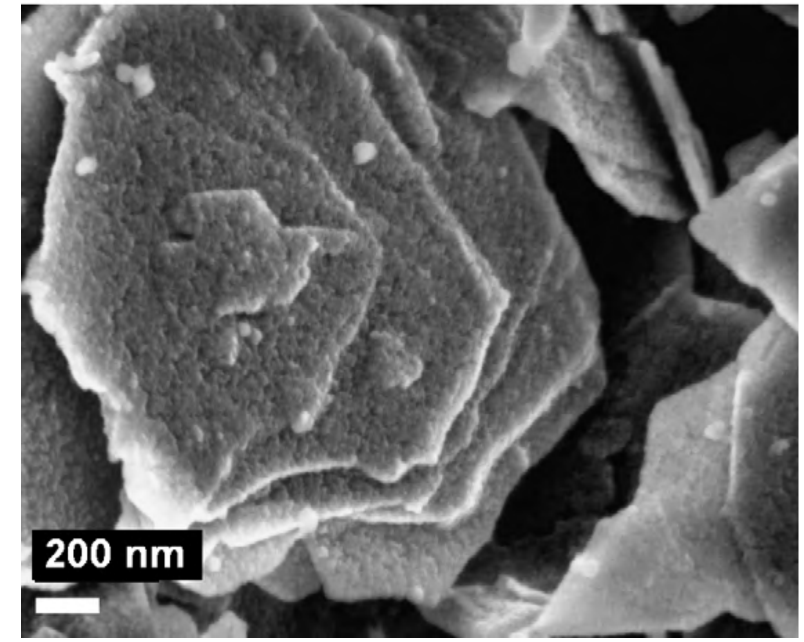


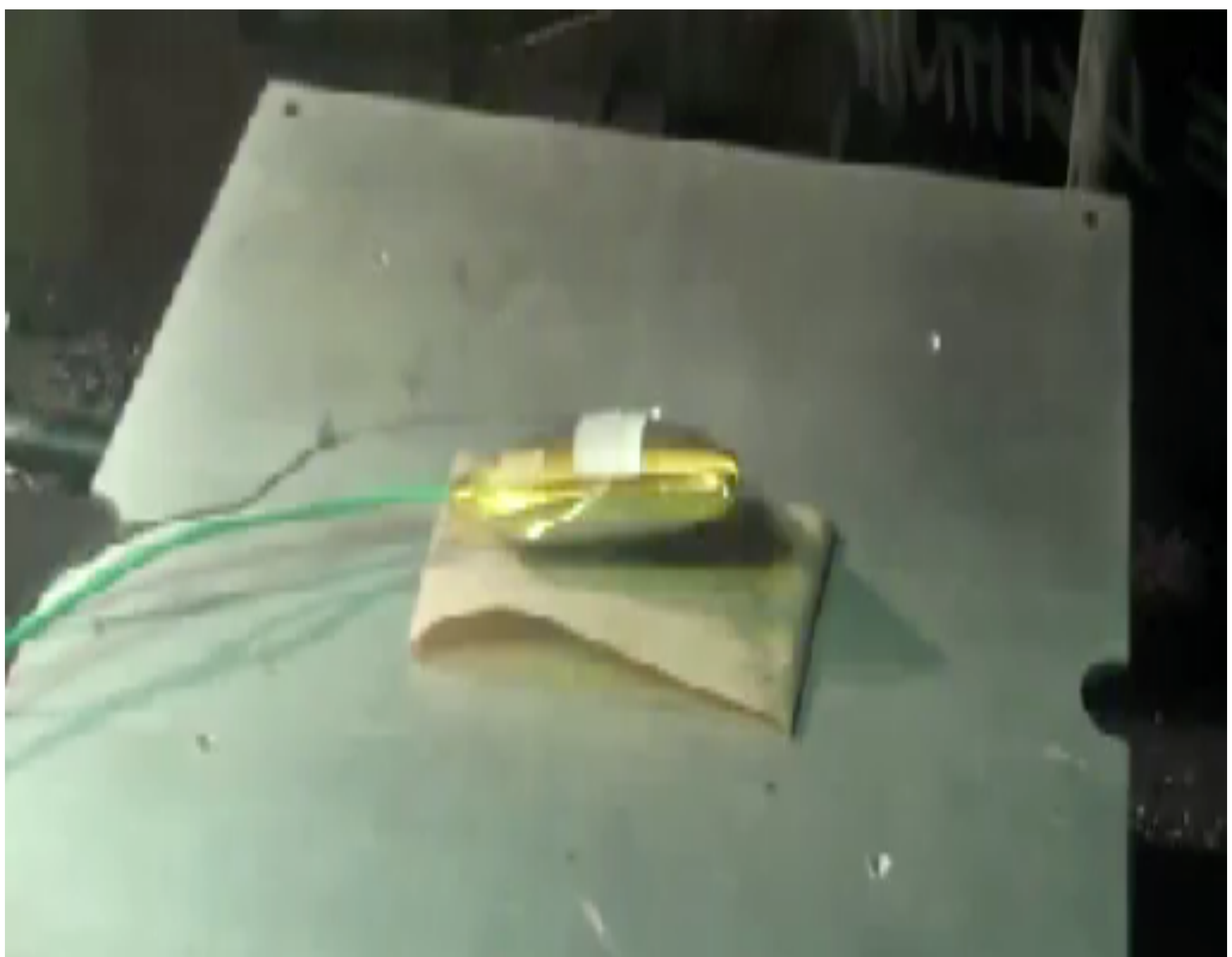
Carbon coatings

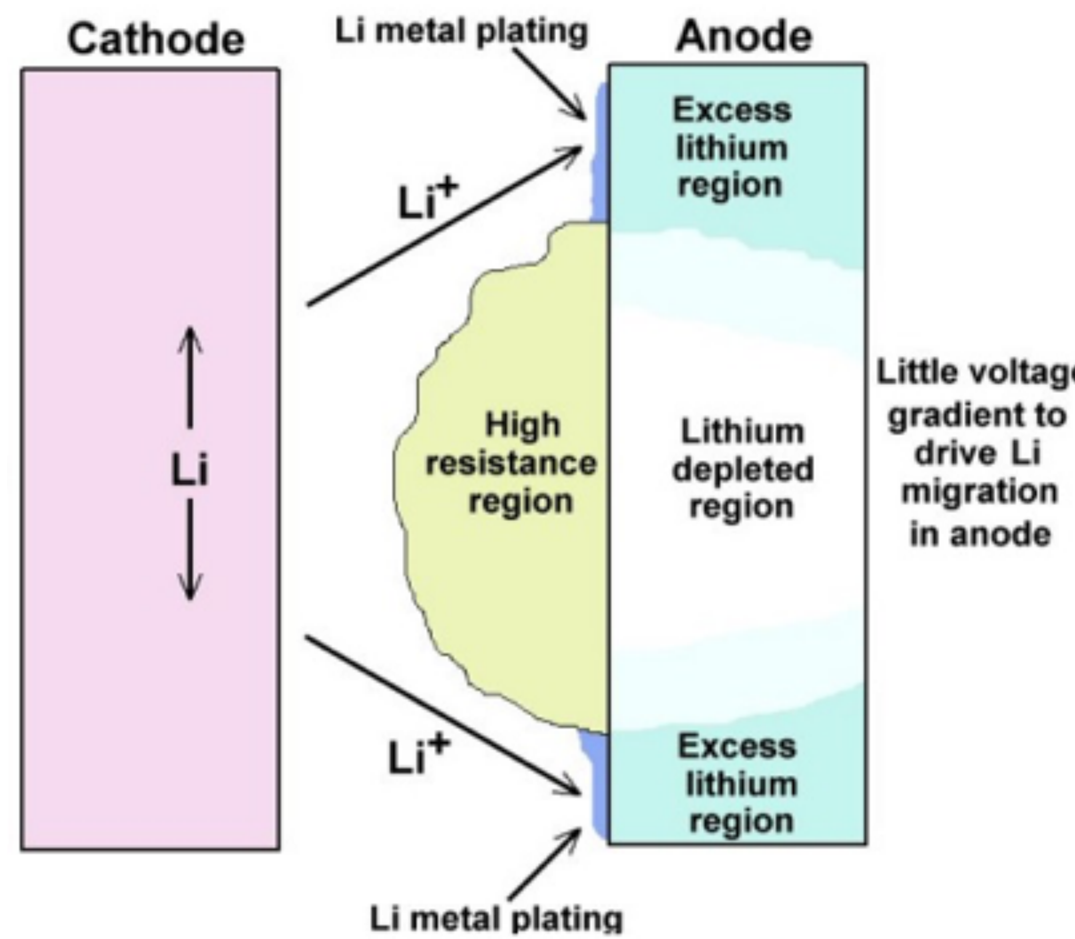




SEI formation







Наноматериалы в ЛИА: за и против

Скорость интеркаляции/экстракции лития:
$\tau = L^2 / D$

Обратимые электродные реакции, которые невозможны в объемных материалах

Высокая удельная площадь поверхности, большая площадь контакта с электролитом, высокий ионный поток

Изменение равновесных потенциалов

Эффективность производства и цена

Проблемы организации хорошего контакта между частицами

Высокая реакционная способность приводит к сторонним реакциям

Малая плотность нанопорошков, уменьшение объемной плотности энергии