Soft Materials
~Application to Artificial Muscle~

Literature Seminar

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06/18/2012

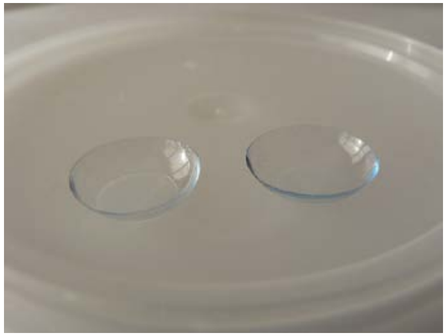
What Is "Gel" ?

Gels are defined as <u>a substantially dilute cross-linked system, which exhibits no flow when in the steady-state.</u>

Ferry, John D. Viscoelastic Properties of Polymers. New York: Wiley, 1980.

Examples of "Gel" around us

Konjak

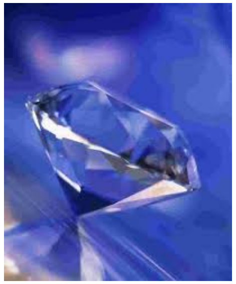


Contact lens

Nappy

Charactaristics of “Gel”

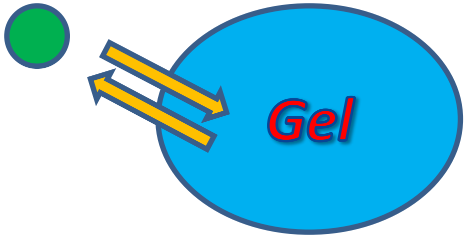
1. Solid + Liquid = “Soft material”



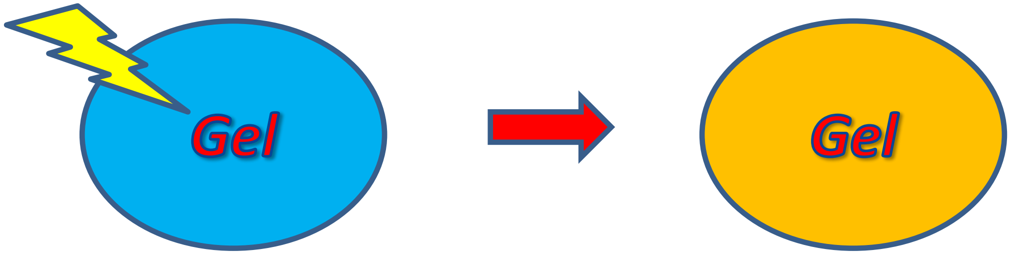
\+

= ??

2. Open system in non-equiliblium state



3. Intelligent function



Today's Topics

1. ***Basic concept and history of "Gel"***

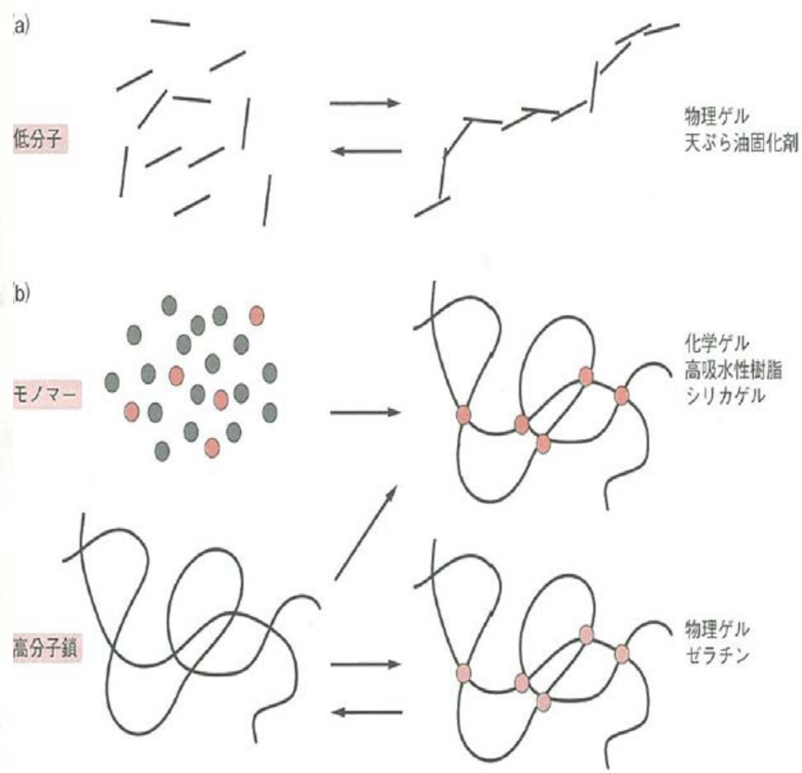
2. ***Application to artificial muscle***

3. ***Future outlook***

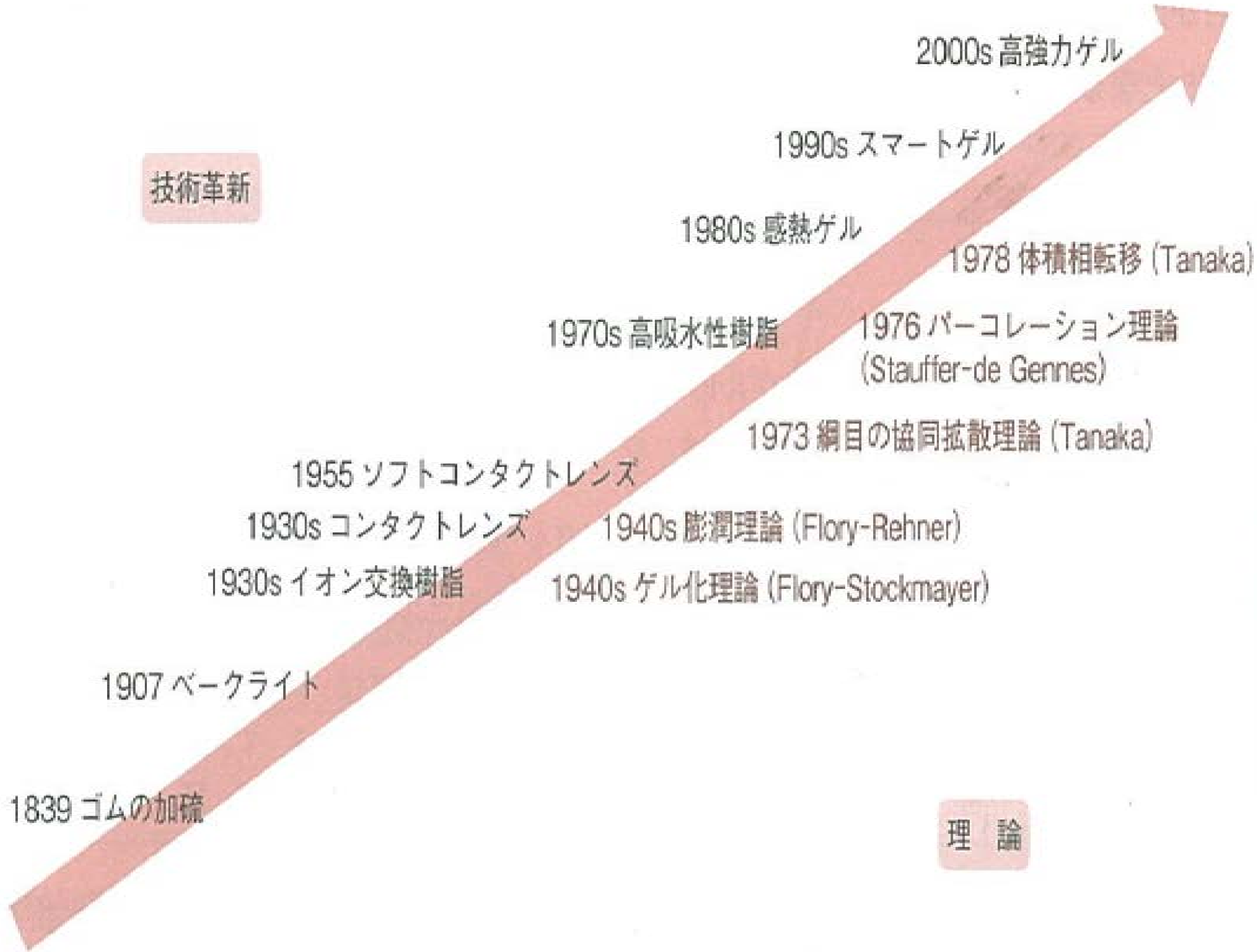
Types of “Gel”

表１　ゲルの分類

架橋方式（準架橋）	共有結合	架橋剤・化学架橋，光・放射線
	クーロン力	高分子電解質
	水素結合	天然ゲル，凍結ゲル
	配位結合	低分子・イオン
	絡み合い	高重合度，分岐，強度は弱い
構成高分子	天然ゲル	食品，タンパク質，多糖，自然界に生きている組織
	ハイブリッドゲル	医用材料，人工皮膚，人工角膜，人工膵臓モデル
	合成ゲル	有機高分子，コンタクトレンズ，高吸水性樹脂，シリカゲル
形態サイズ	ミクロゲル	分子内架橋，巨大化しない
	マクロゲル	分子間架橋，通常のゲル
溶　媒	空気	エーロゲル，キセロゲル
	水	ヒドロゲル
	油性	リポ（オルガノ）ゲル

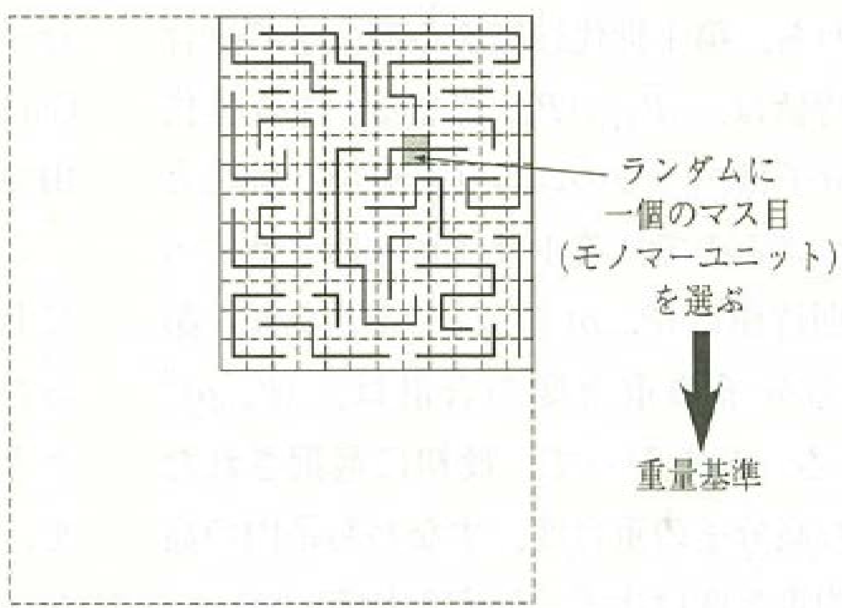


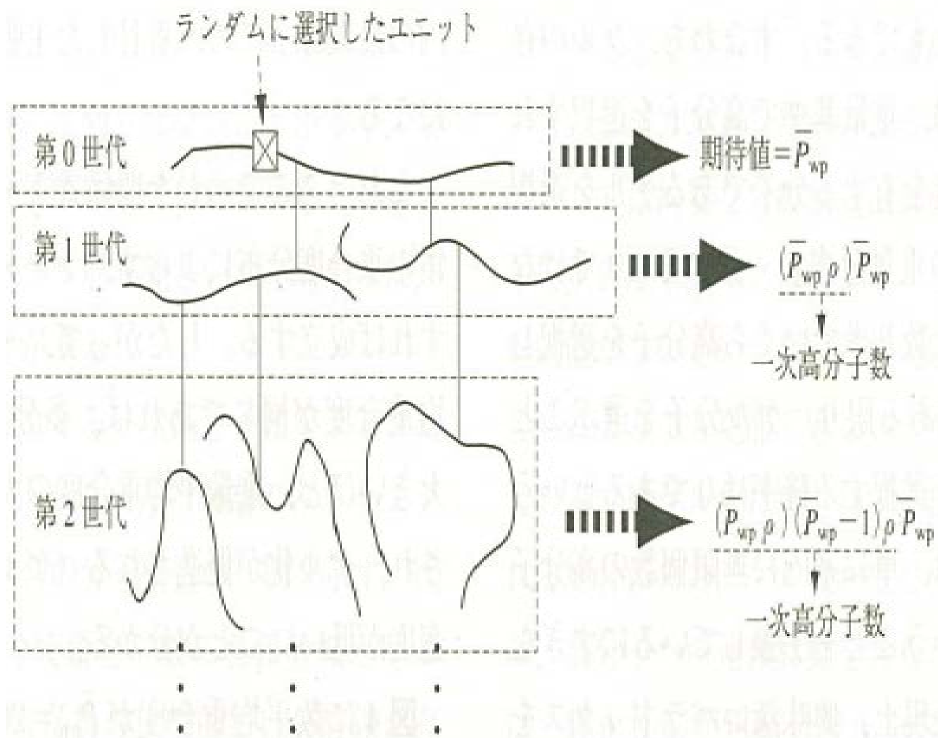
History of “Gel”



Evaluation of Gel Point

Flory-Stockmayer model





$$\bar{P}_w = \bar{P}_{wp} + (\bar{P}_{wp})^2 \rho \sum_{i=0}^{\infty} \left\{ (\bar{P}_{wp}-1)\rho \right\}^i$$

$$= \frac{\bar{P}_{wp}(1+\rho)}{1-(\bar{P}_{wp}-1)\rho} \qquad \text{(1a)}$$

$$\cong \frac{\bar{P}_{wp}}{1-\bar{P}_{wp}\rho} \qquad (\bar{P}_{wp} \gg 1 \text{ かつ } \rho \ll 1 \text{ の場合}) \quad \text{(1b)}$$

ゲル化点 =重量平均重合度無限大

$$\rho = 1/\bar{P}_{wp}$$

Osmotic Theory of Gel

ゲル網目の変形に伴うギブス自由エネルギーの変化

$\Delta G = \Delta G_m + \Delta G_e$

ΔG_m 網目と溶媒との混合からの寄与

ΔG_e 弾性からの寄与

$\Delta G_m = k_B T[n_1 \ln v_1 + n_2 \ln v_2 + \chi n_1 v_2]$

k_B:ボルツマン定数、n_1 :溶媒分子数、n_2 :高分子鎖数

v_1:溶媒の体積分率、v_2:溶媒の体積分率

χ :高分子-溶媒相互作用パラメータ

$\Delta G_e = (3/2)\, k_B T v_e\, (\alpha^2 - 1 - \ln\alpha)$

v_e:実在の網目中における鎖の有効数、α :変形因子

$$\Delta G = n_1 k_B T[\ln v_1 + \chi v_2] + (3/2)\, k_B T v_e\, (\alpha^2 - 1 - \ln\alpha)$$

(n_2 =1よりn_2を含む項は無視できる)

Osmotic Theory of Gel

化学ポテンシャル変化

$\Delta\mu_1 = N_A(\partial\Delta G_m/\partial n_1)_{T,\,p} + N_A(\partial\Delta G_e/\partial\alpha)_{T,\,p}\,(\partial\alpha/\partial n_1)_{T,\,p}$

$\quad = \mathbf{RT[\ln v_1+v_2+\chi v_2^{\,2}+V_1(v_e/V_0)(v_2^{\,1/3}-v_2/2)]}$

V_0:高分子網目の膨潤前体積、V_1:溶媒のモル体積

$\alpha^3 = V/V_0 = 1/v_2$ (V:高分子網目の膨潤体積)

平衡膨潤状態のとき、$\Delta\mu_1 = 0$

Equation of State of Gel

浸透圧

$\pi = -\Delta\mu_1/V_1 = -(RT/V_2)[\ln(1-v_2)+v_2+\chi v_2{}^2]+RT(v_e/V_0)(v_2/2-v_2{}^{1/3})$

$= \ldots$

$\mathbf{= -(NkT/v)[\phi+\ln(1-\phi)+(\Delta F/2kT)\phi^2]+\nu kT[\phi/2\phi_0-(\phi/\phi_0)^{1/3}]+f\nu kT(\phi/\phi_0)}$

= (網目高分子と溶媒の混合による圧力)+(弾性による圧力)+
(対イオンによる圧力)

ただし$R = kN$, $V_1 = v$, $v_2 = \phi$, $\chi = \Delta F/2kT$, $v_e/V_0 = \nu$,
f: 架橋点高分子鎖一本当たりの解離している対イオンの数

平衡状態($\pi = 0$)において$\tau = 1-(\Delta F/kT)$と定義すると、

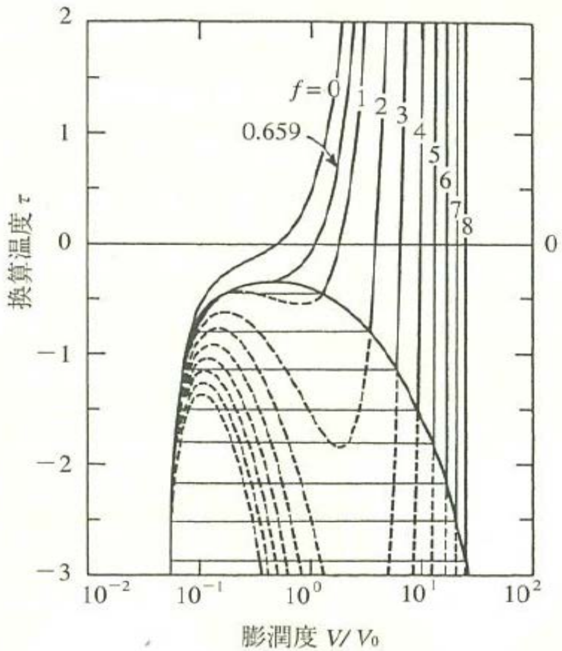
$\boldsymbol{\tau = -\nu v/N\phi^2\,[(2f+1)\,(\phi/\phi_0)-2\,(\phi/\phi_0)^{1/3}\,]+1+2/\phi+[2\ln(1-\phi)]/\phi^2}$

$(V/V_0 = \phi_0/\phi)$

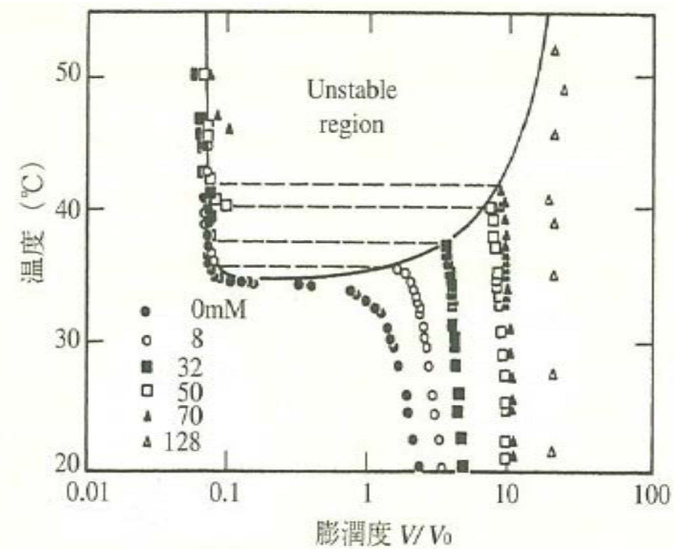
Volume Phase Transition

$$\tau = -\nu v/N\phi^2\,[(2f+1)\,(\phi/\phi_0)-2\,(\phi/\phi_0)^{1/3}\,]+1+2/\phi+[2\ln(1-\phi)]/\phi^2$$

$(V/V_0 = \phi_0/\phi,\ \tau = 1-(\Delta F/kT))$



ゲルの理論的膨潤曲線（f は架橋点間の高分子鎖 1 本当たりの対イオンの数を表す）5)

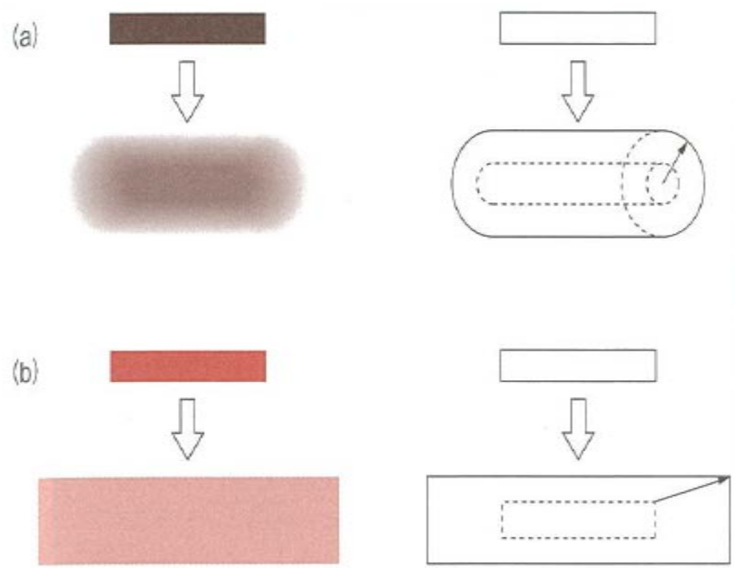


N-イソプロピルアクリルアミド/アクリル酸ナトリウム共重合体ゲルの水中での膨潤曲線．数字はアクリル酸ナトリウムの濃度を表す6)

体積相転移: 温度や溶媒組成などの外部条件の連続的な変化に応じて、ゲルの平衡膨潤度(体積)が大きな不連続変化を示す現象

T. Tanaka, *Phys. Rev. Lett.*, **1978**, *40*, 820.

Kinetics of Osmotic Theory



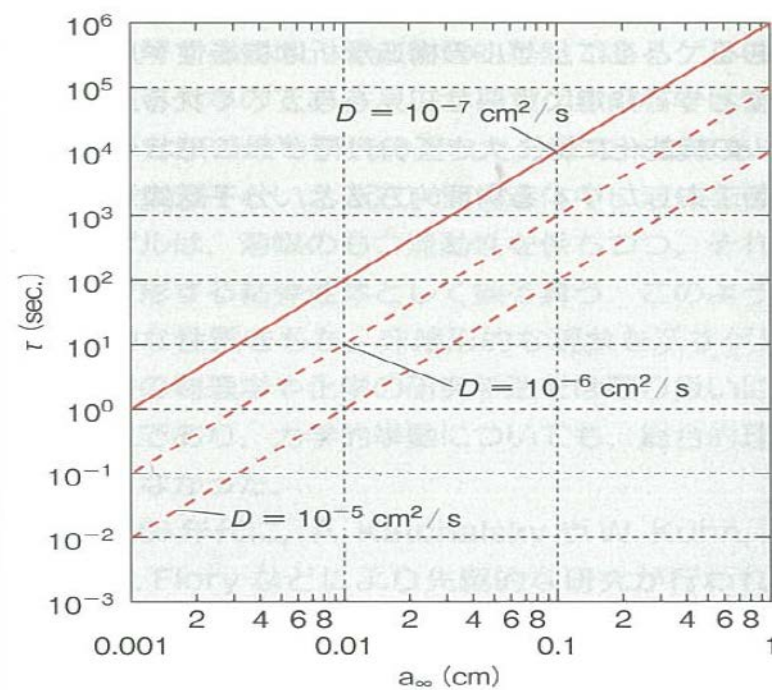
(a) ink: diffusion (b) gel

膨潤の緩和時間

$\tau = \mathbf{a^2/\pi^2 D}$

a:半径、

D:ポリマー網目の拡散係数



Summary of First Topic

Gel is essential for our life.

Volume phase transition
(1978 T.Tanaka)

→

Explosive development
In the field of gel chemistry !!
(intelligent gel, actuator…)

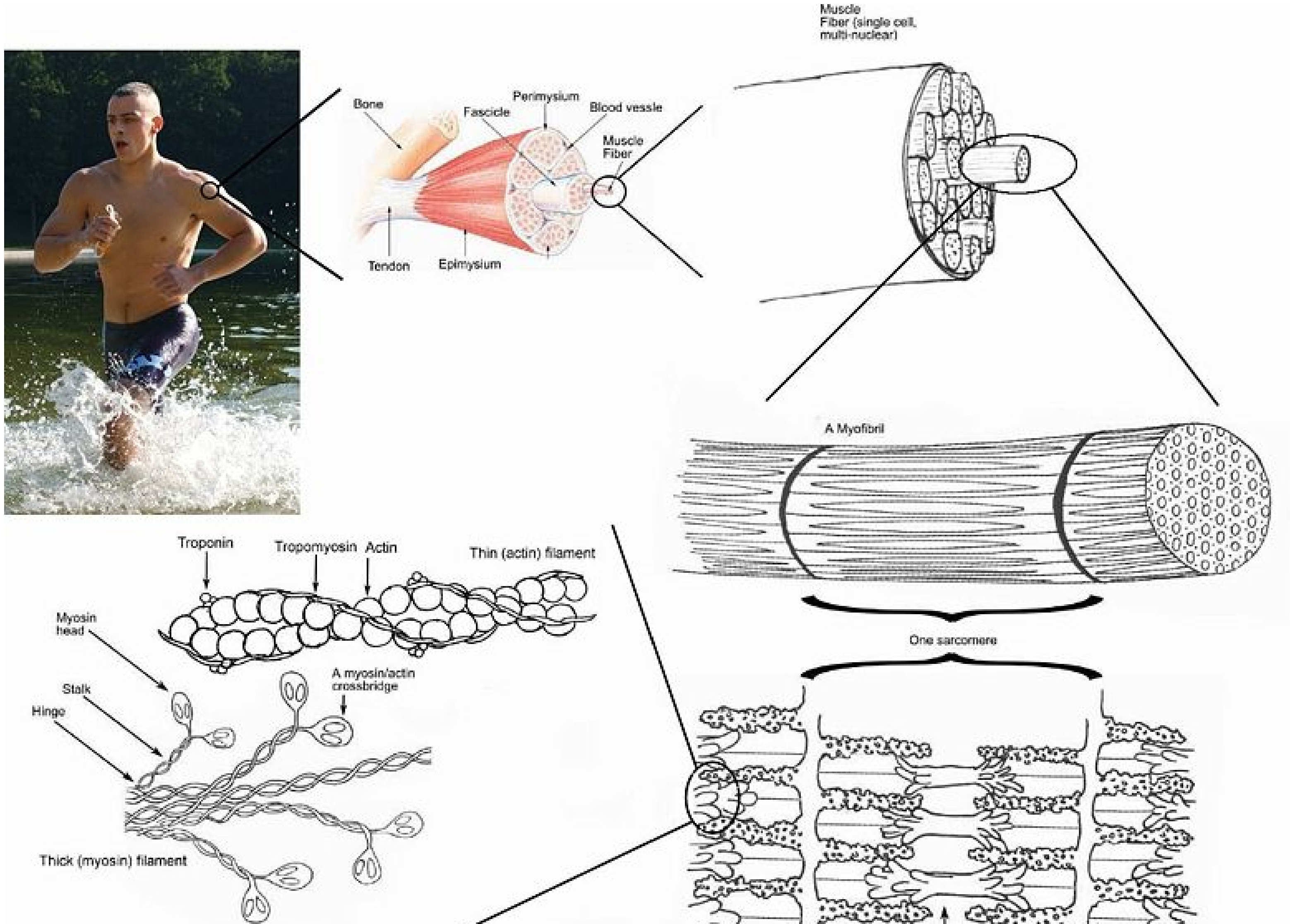
Today's Topics

1. *Basic concept and history of "Gel"*

2. *Application to artificial muscle*

3. *Future outlook*

The Structure of Muscle



Chemical reactions produce ATP molecules which are used to power the movement of the myosin heads.

Artificial Muscle

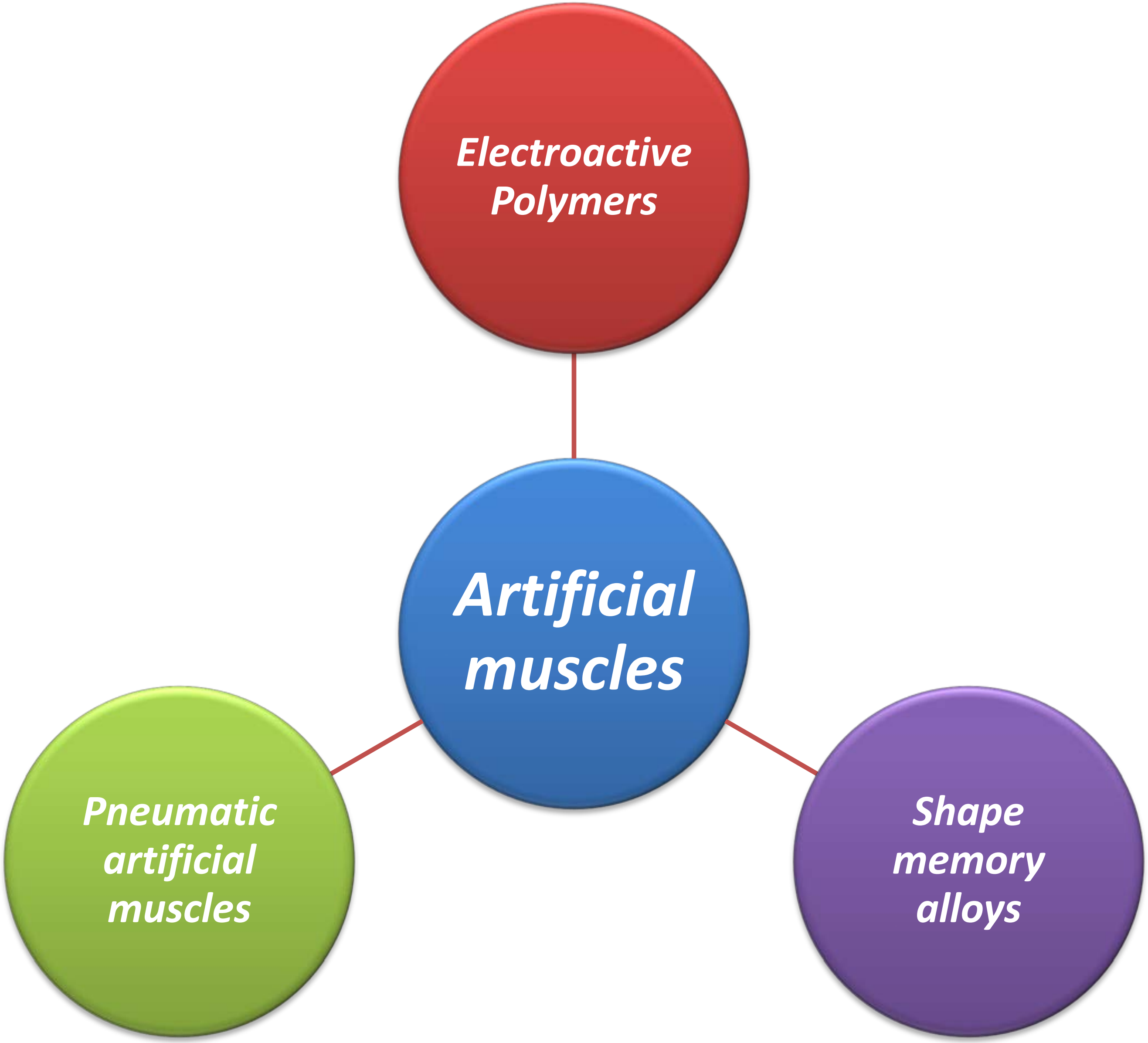
Artificial muscle: actuators which mimic the muscles in our own human bodies

Actuator: type of motor for moving or controlling a mechanism or system.
It is operated by a source of energy, usually in the form of an electric current, hydraulic fluid pressure or pneumatic pressure, and converts that energy into some kind of motion.

Functions needed for artificial muscles:

1. ***High compliance, flexiblity***
2. ***High power density, small***
3. ***Compact, mobile***

Types of Actuators



Pneumatic Artificial Muscles

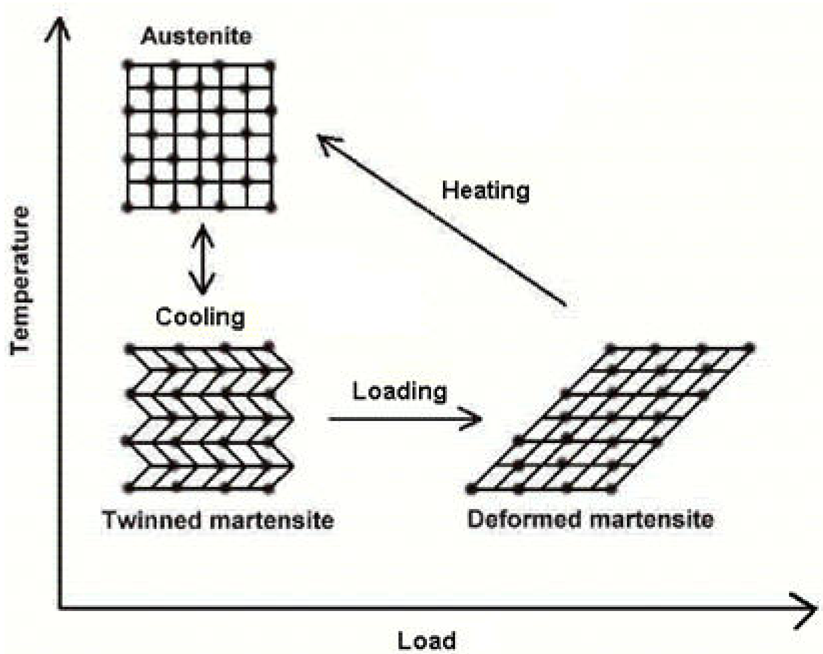
Pneumatic artificial muscles (PAMs) :
contractile or extensional devices operated by pressurized air filling a pneumatic bladder.

Problems:

1. ***These systems require air compressors that are neither light nor small.***
2. ***Their response speed is limited by the ability of compressors.***
3. ***Consumable***

Shape Memory Alloys

Shape-memory alloys (SMAs):
an alloy that "remembers" its original, cold-forged shape: returning the pre-deformed shape by heating.



Problems:
1. ***It takes time to cool the alloy and return to the rest position.***
2. ***Low efficiency***

Types of Actuators

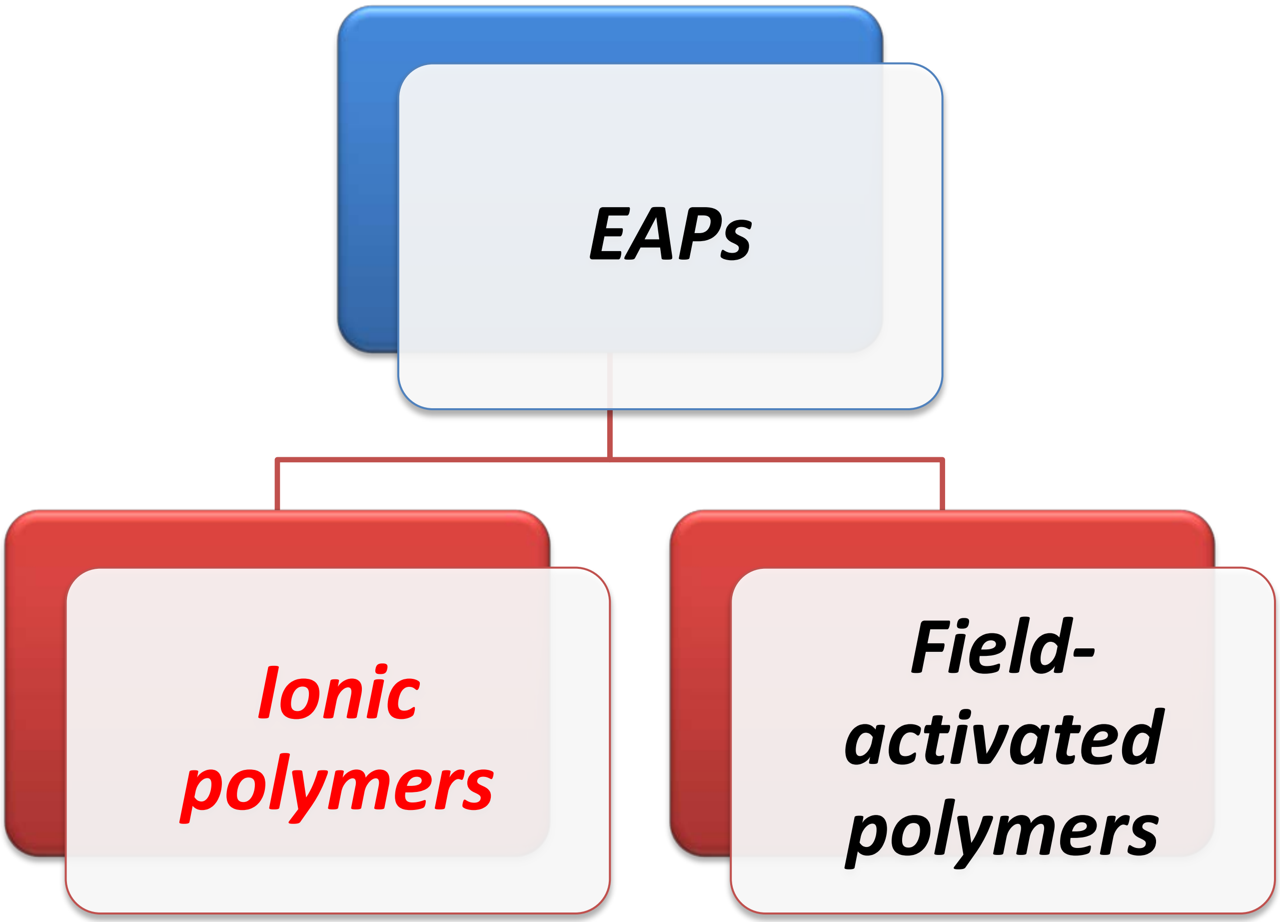
	Compliance	*Power density*	*Mobility*
Electroactive polymes	***Very good***	***Not so good***	***Possible***
Penaumatic artificial muscles	*Good*	*Very good*	*Difficult*
Sharp memory alloys	*Good*	*Good*	*Possible*

(also see appendix for detail values)

Electroactive polymers are being developed as a prominent candidate of artificial muscles !!

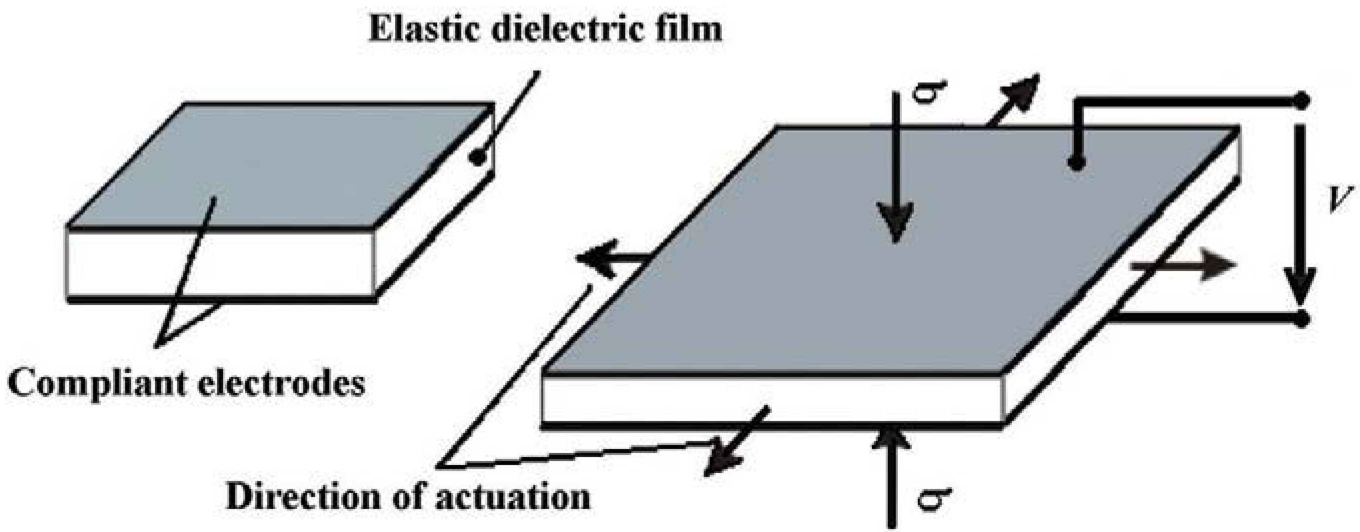
Electroactive Polymers (EAPs)

Electroactive Polymers (EAPs):
polymers that exhibit a change in size or shape when stimulated by an electric field.



Field-Activeted Polymers

Dielectronic elastomers

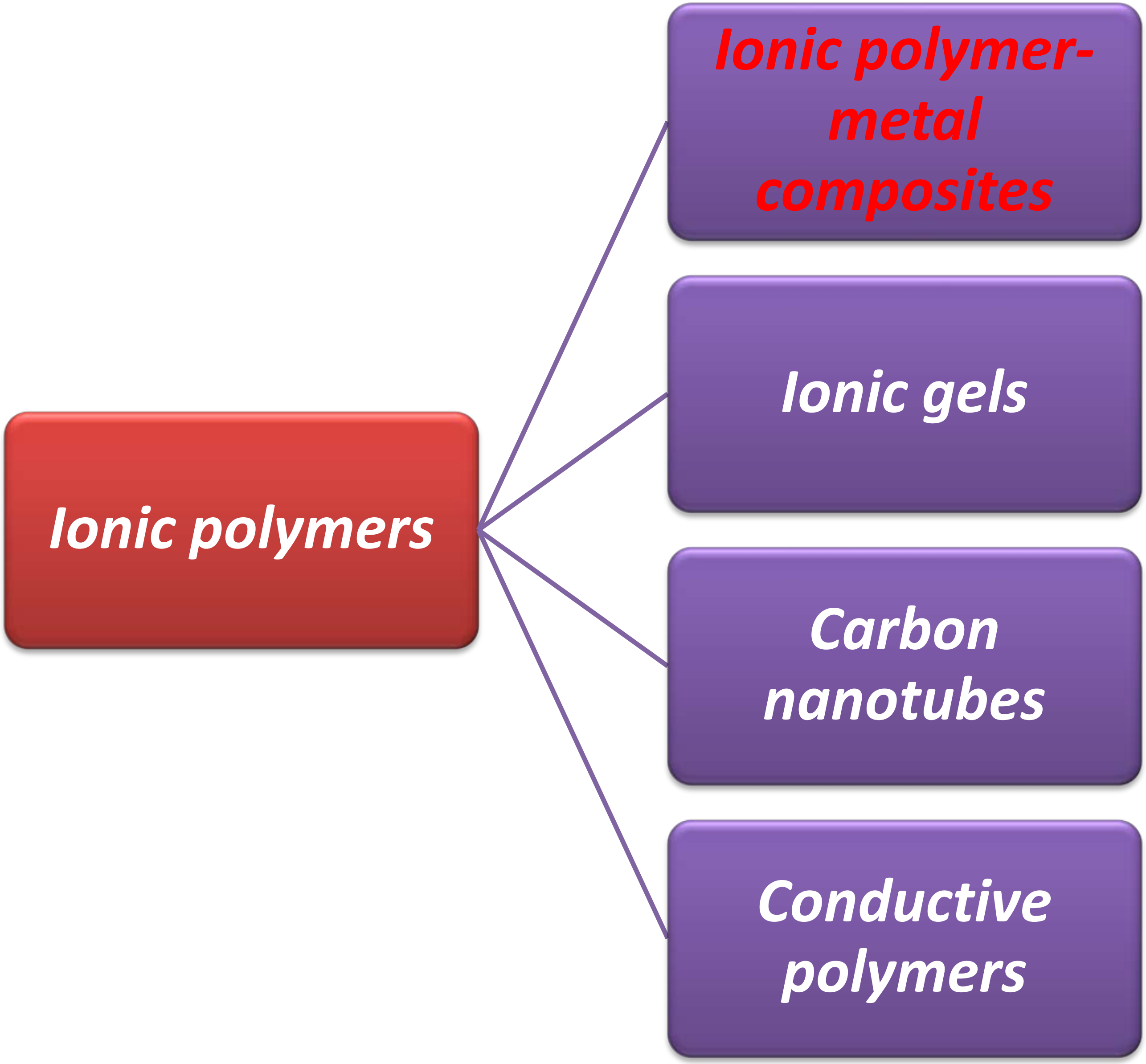


When a voltage is applied across these materials, the attraction between opposite charges and the repulsion of like charges generates stress in the dielectric, known as Maxwell stress, which compresses and elongates the dielectric.

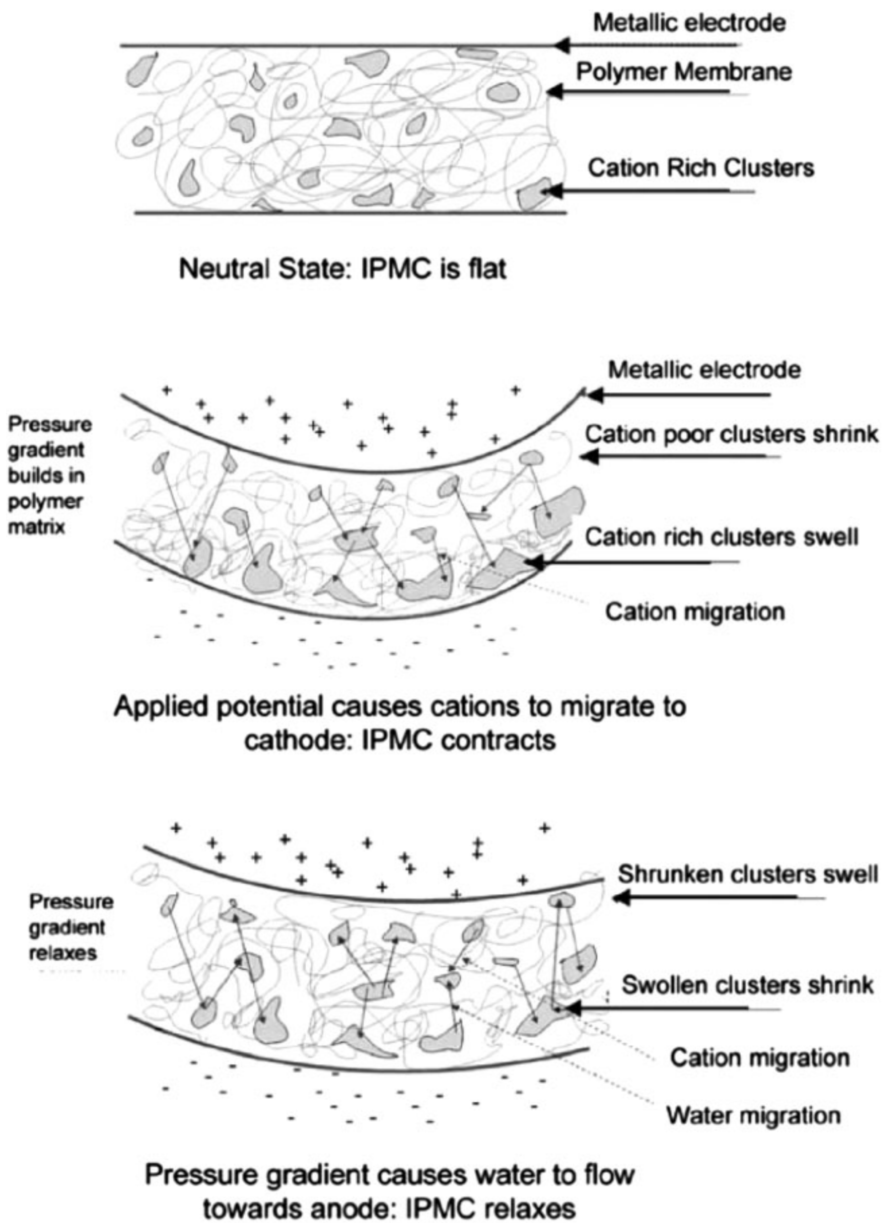
DEs are one of the most studied polymer actuators and numerous applications are being developed.
(electroactive fluid pumps, conformal skins for Braille screens, insect-like robots, and Artificial Muscles' autofocus lens positioner)

Mat. Today. **2007**, *10*, 30.

Ionic Polymers



Ionic Polymer-Metal Composites



IPMCs consist of a solvent swollen ion-exchange polymer membrane laminated between two thin flexible metal or carbon-based electrodes

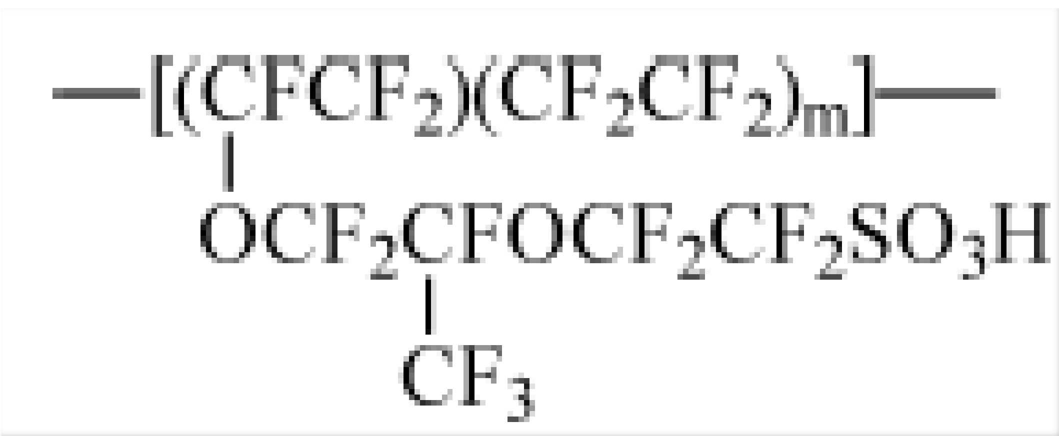
General basic ion exchange polymer: Perfuluorinated alkanes with side-chains terminated by ionic group

Ex) Nafion from DuPont

Nafion

Nafion :sulfonated tetrafluoroethylene based fluoropolymer -copolymer discovered in the late 1960s by Walther Grot of DuPont.

Structure of Nafion

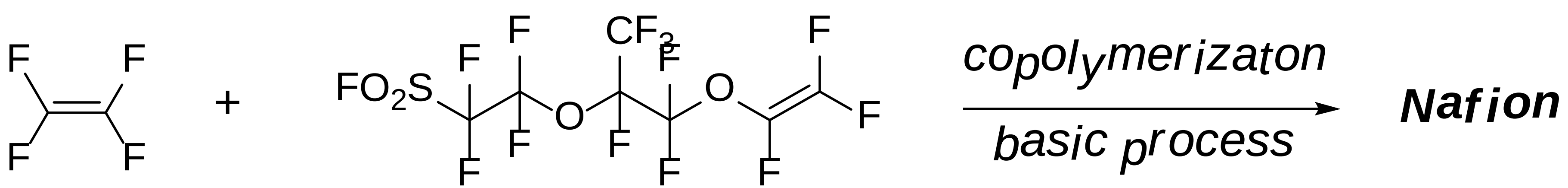


State of Understanding of Nafion
Chem. Rev. **2004**, *104*, 4535.

Synthesis

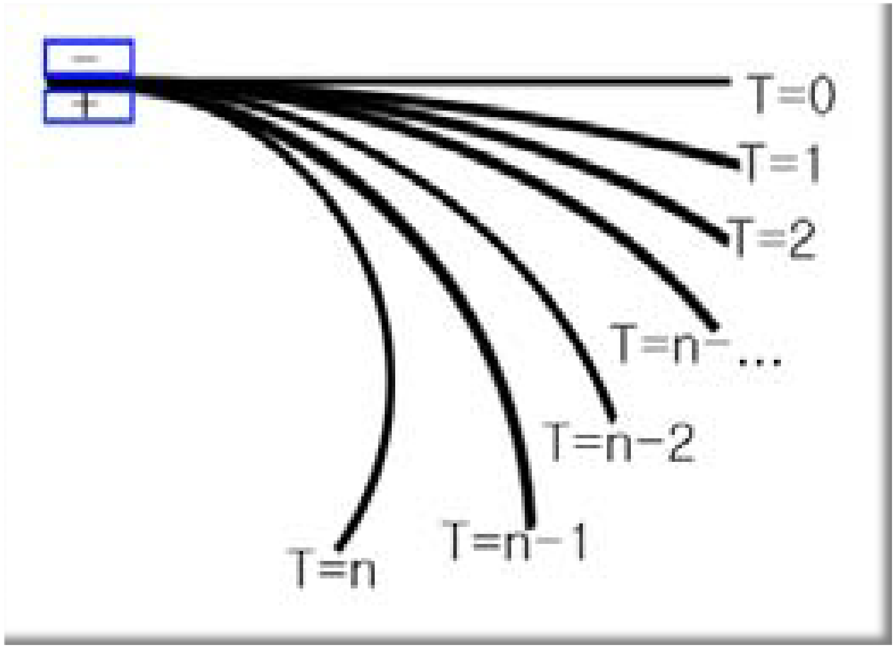
Preparation

copolymerization of tetrafluoroethylene (TFE) and a derivative of a perfluoro (alkyl vinyl ether) with sulfonyl acid fluoride.



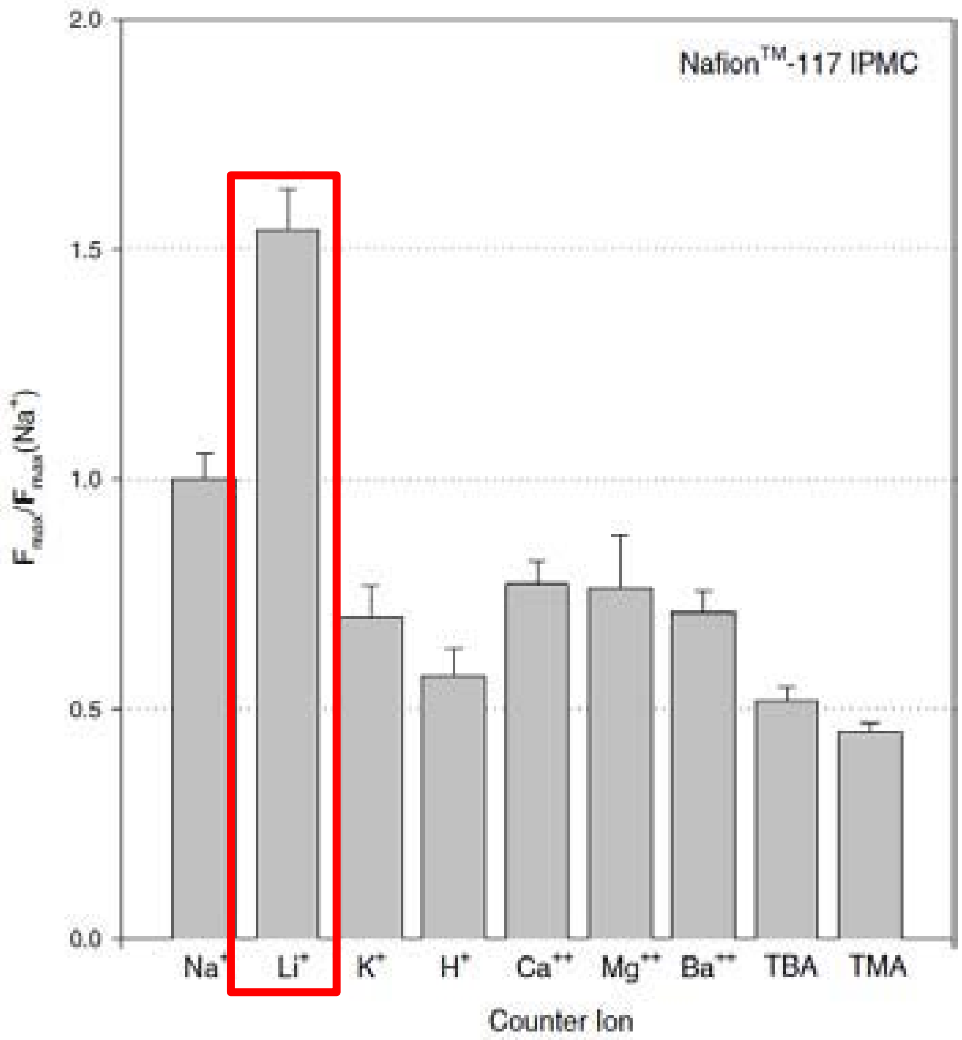
Synthesis of perfluorinated vinyl ether monomer: see appendix

Typical Bending Response of IPMC



When a water-saturated cantileverd strip of Nafion-based IPMC is subjected to a small DC Potential, it undergoes a fast bending deformation towards the anode, followed by a slow relaxation in the opposite direction.

Effect of Different Cations



Effect of various cations on blocking force

Ionic Hydration Effect

Result of IR analysis

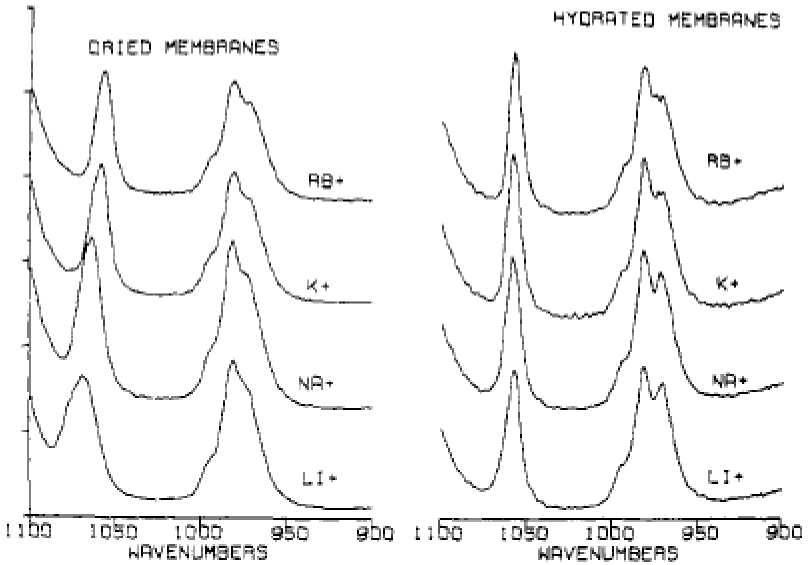


Figure 3. Infrared spectra of the $-SO_3^-$ symmetric stretch region from Nafion films in the Li^+, Na^+, K^+, and Rb^+ salt forms.

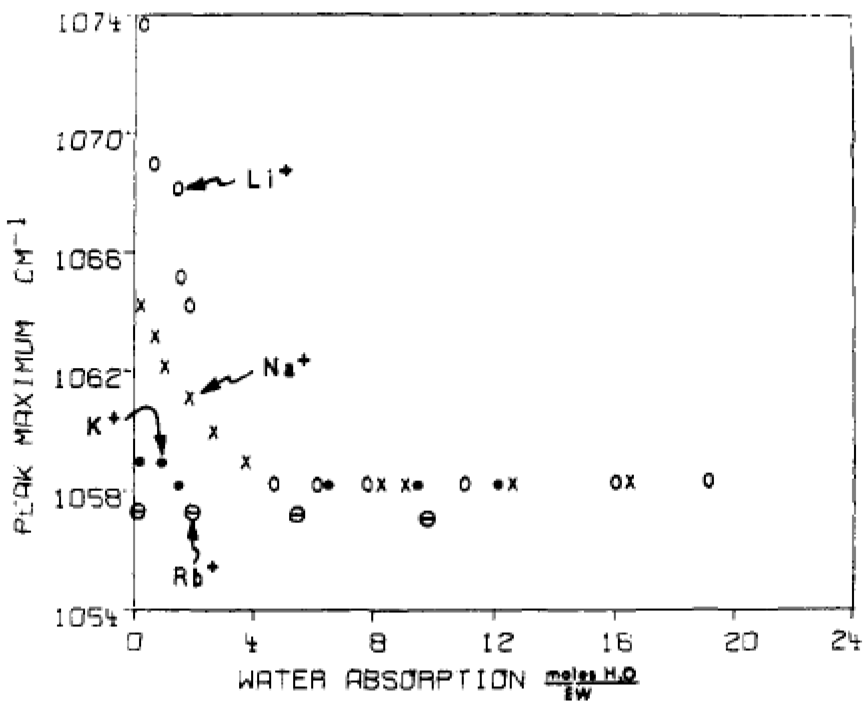


Figure 5. Plots of the $-SO_3^-$ symmetric stretch peak maxima as a function of the H_2O/SO_3^- mole ratio for the Rb^+, K^+, Na^+, and Li^+ salts of 1100 EW Nafion.

J. Am. Chem. Soc. **1980**, *102*, 4665.

Ionic Hydration Effect

Four-state model

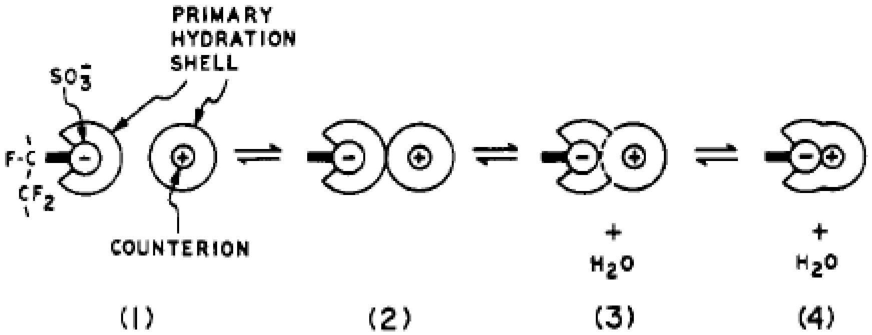


Figure 6. Four-state model of the hydration-mediated dissociation equilibrium between unbound and side chain associated counterions in Nafion membranes.

1. **Completely dissociated hydrated ion pairs**
2. **Ion pairs at the contact of undisturbed primary hydration shells**
3. **Outer-sphere complexes**
4. **Inner-sphere complexes**

Lithium ion: stronger electrostatic field
large hydration sphere

J. Am. Chem. Soc. **1980**, *102*, 4665.

Performance Improvement

1. ***Solvent loss in IPMC (electrolysis and evaporation)***

2. ***Lowering surface resistance of IPMC surface electrode (gold coating)***

3. ***Encapsulation of IPMC***

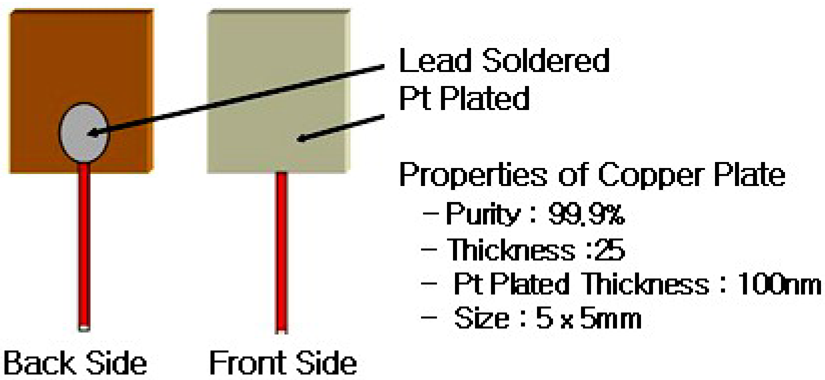
4. ***Structure of membrane***

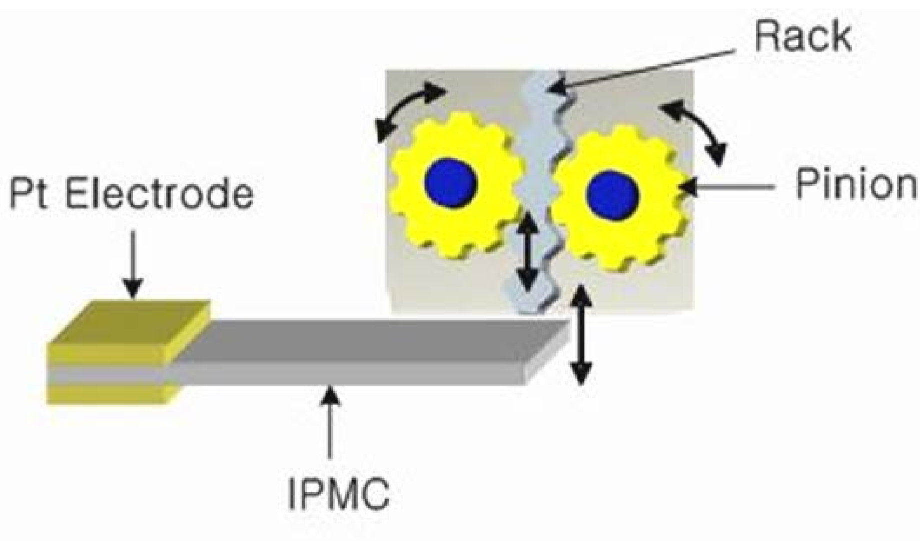
Etc…

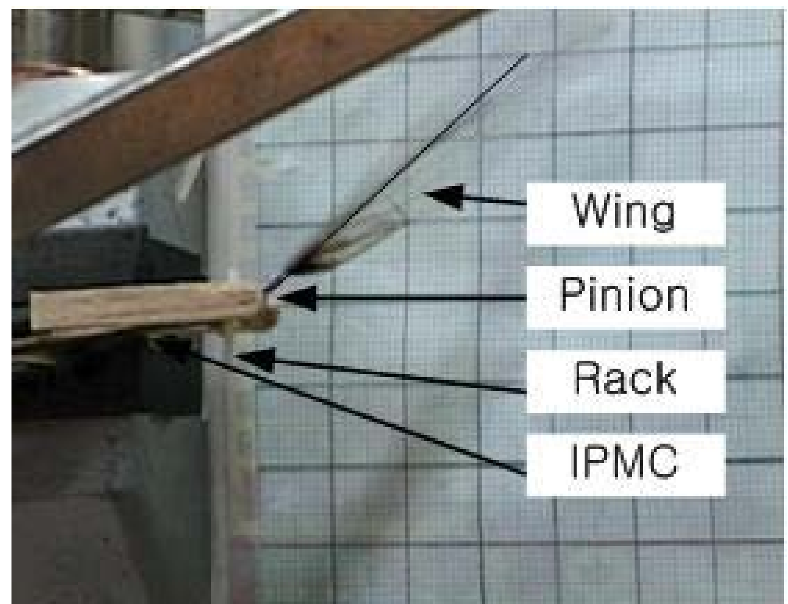
Int. J. Control. Autom. Syst. **2006**, *4*, 748.
International Journal of Precision Engineering and Manufacturing. **2012**, *13*, 141.

Mechanical Applications

Flapping device



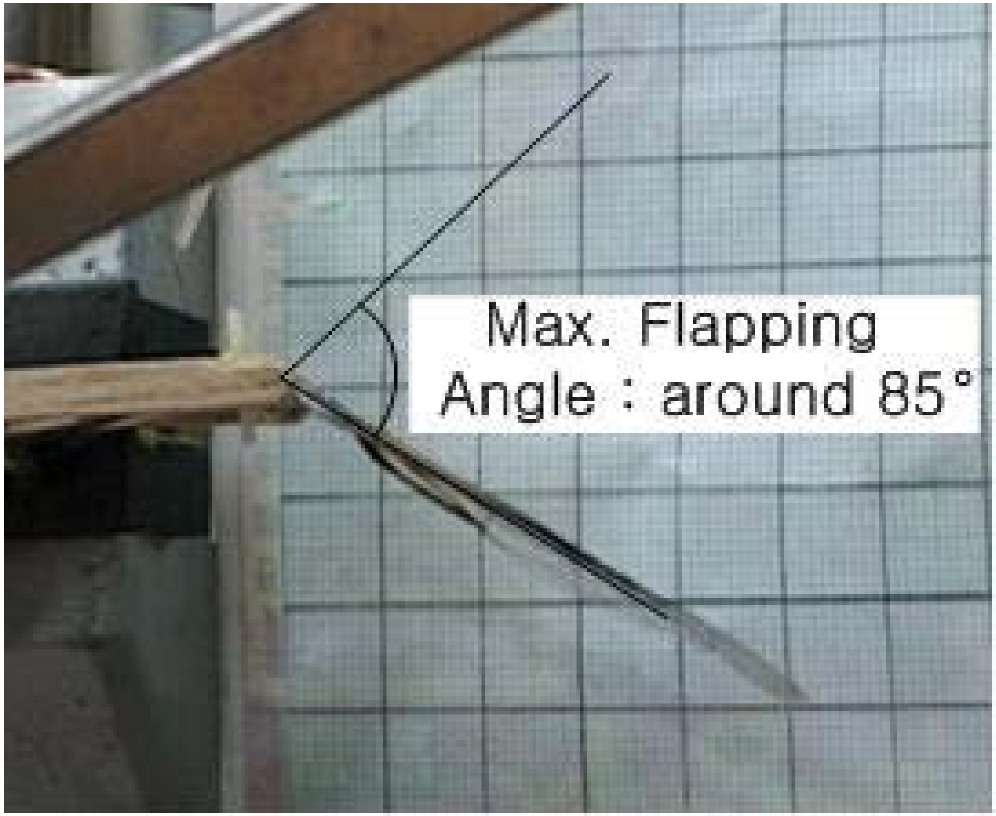




Int. J. Control. Autom. Syst. **2006**, *4*, 748.

Mechanical Applications

Flapping device



Applied voltage: 3~4 V
Square wave form: 0.5~10 Hz

Maximum flapping angle: 85 degree (1 Hz input)

Flapping angle: 15 degree (3V, 15 Hz input)

The flapping device should be useful for mimicking an insect flying at low frequency.

Int. J. Control. Autom. Syst. **2006**, *4*, 748.

Mechanical Applications

IPMC valve-less micro pump

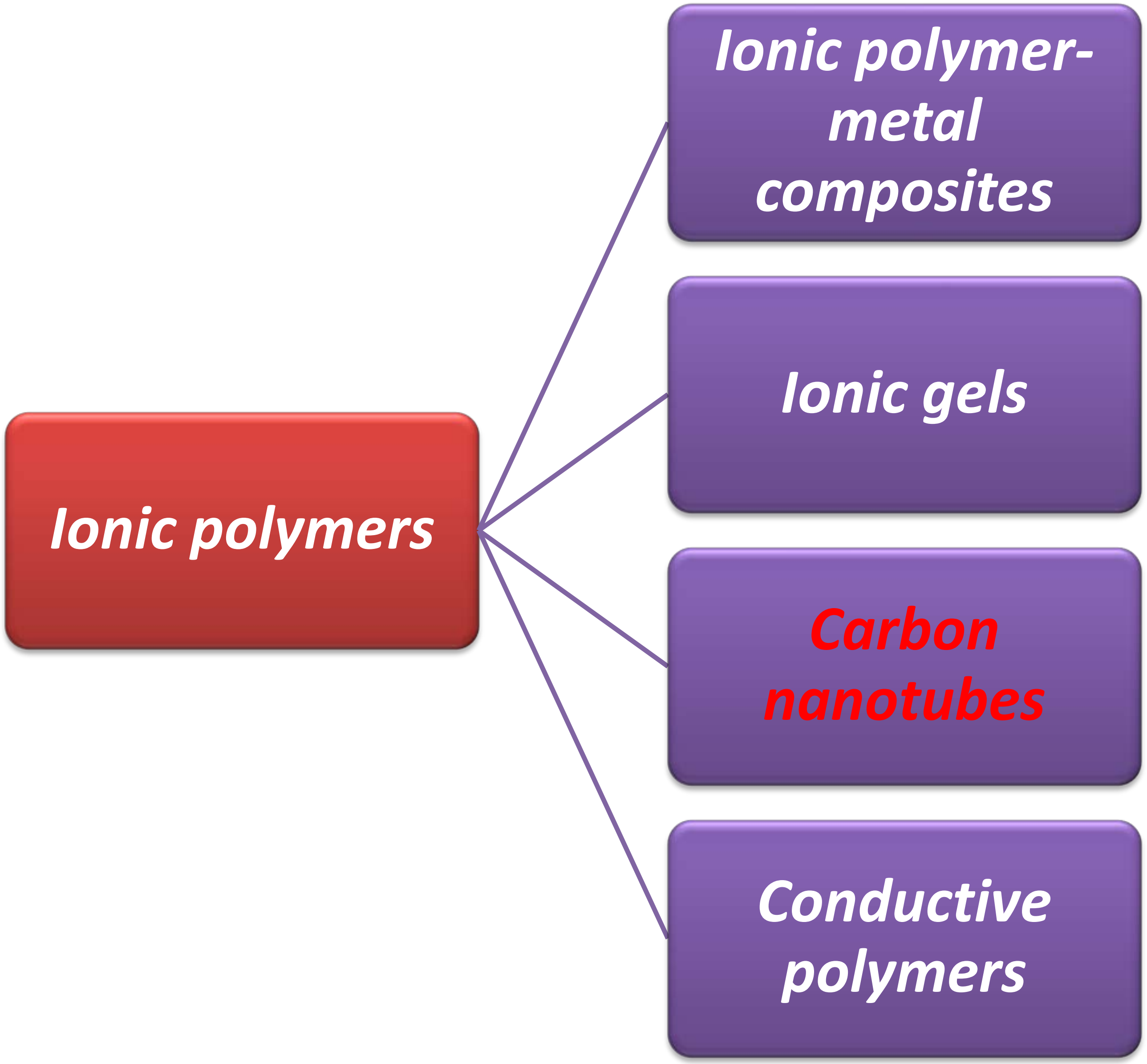
Biomimetic jellyfish robot

Mechanical gripper

Fish robot (developed by Eamax, a Japanese company)

etc…

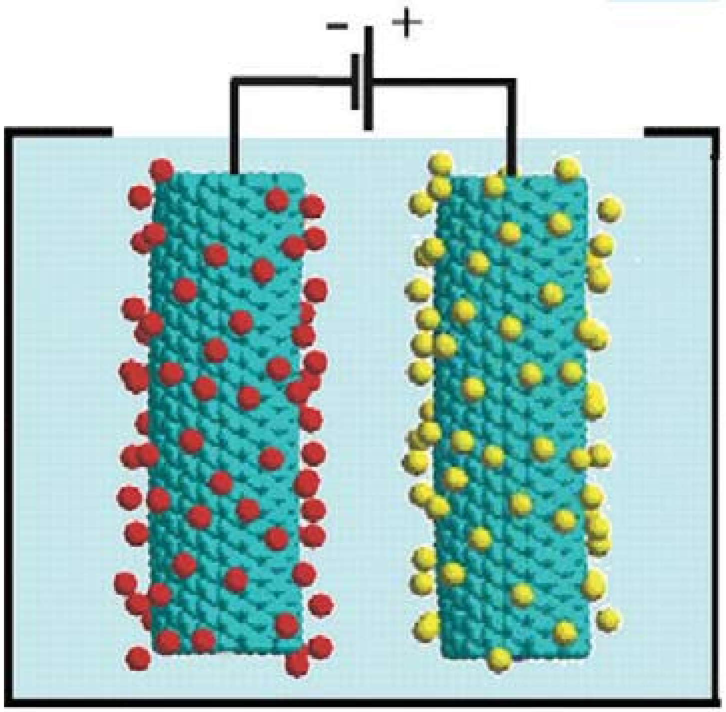
Ionic Polymers



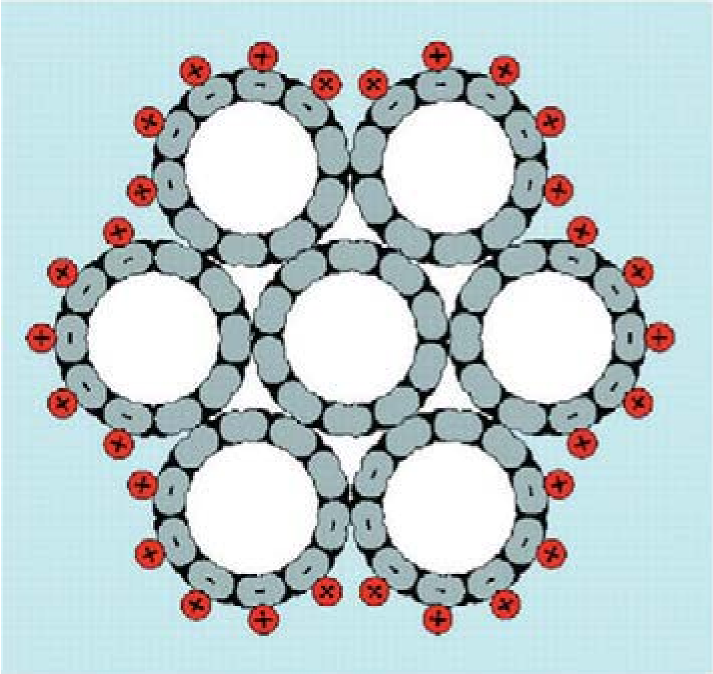
Carbon Nanotube Actuators

***Carbon nanotubes**: very good conductors of both electricity and heat*

very strong and elastic molecules in certain directions
tensile modulus (640 GPa), tensile strength (20-40 GPa)



An applied potential injects charge in the Two nanotube electrodes in solution



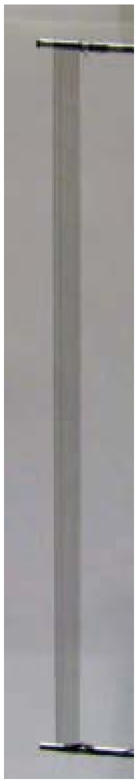
Charge injection at the surface of a nanotube bundle

Coulombic forces resulted in actuation !!

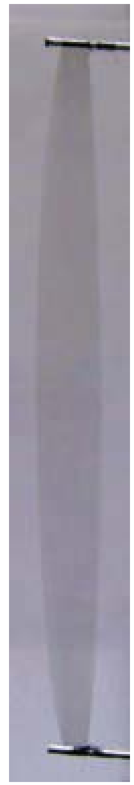
Science. **1999**, *284*, 1340.

Carbon Nanotube Aerogel Muscles

Actuation in sheet width



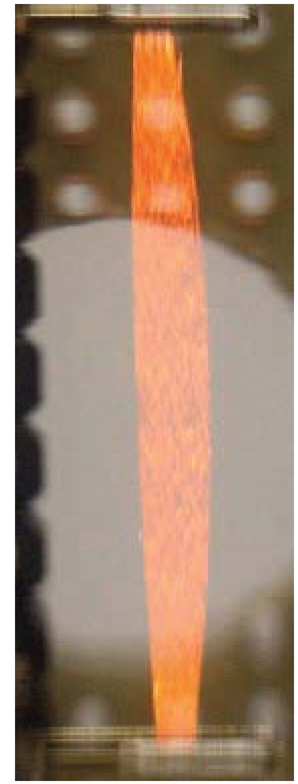
50-mm-long 2-mm-wide nanotube aerogel sheet



Applying a field of 5kV

width: 220% elongation !!

(3.7*10^{4})% per second

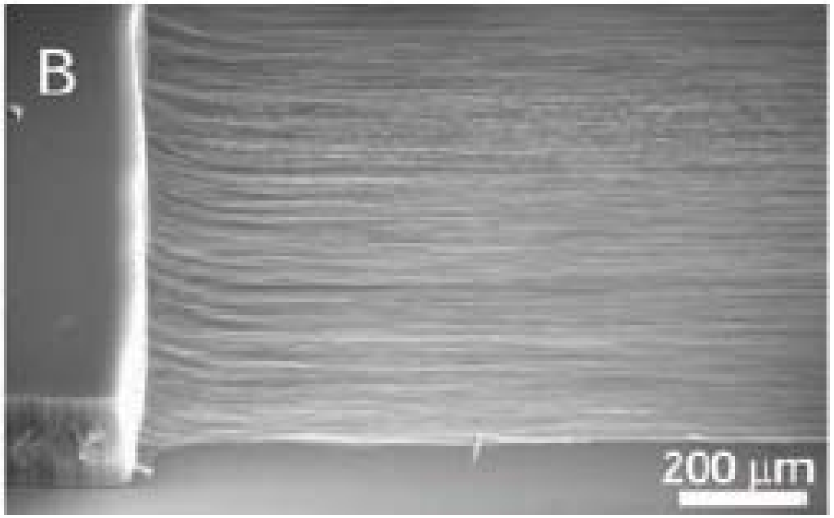


25-mm-long nanotube sheet (***1500 K*** by applying 3kV)

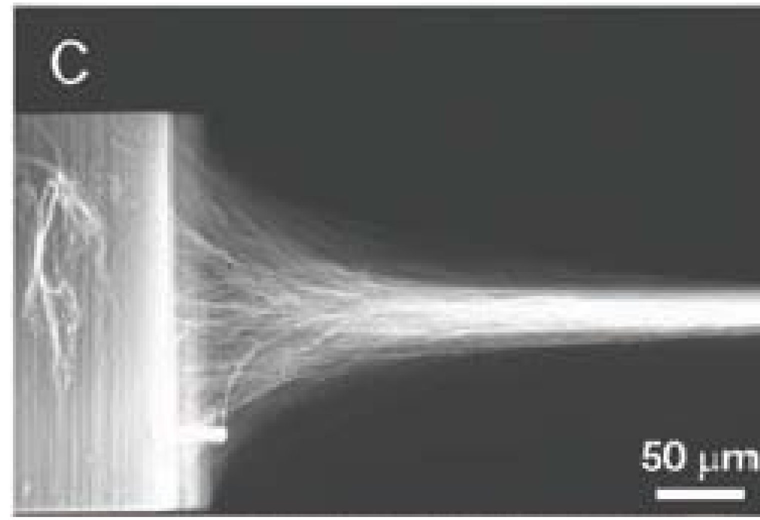
Science. **2009**, *323*, 1575.

Carbon Nanotube Aerogel Muscles

Carbon nanotube sheet



Carbon nanotube forest plane



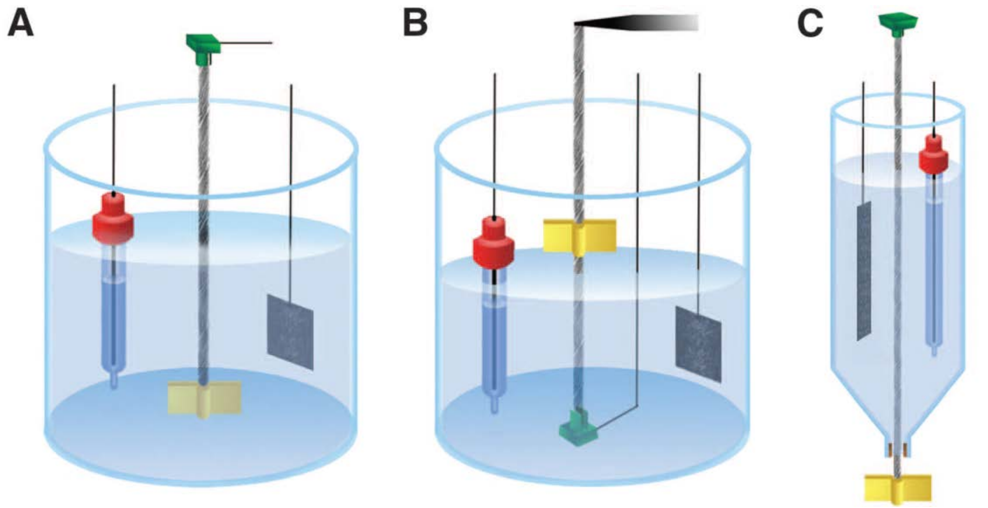
90 degree rotation of MWNTs in a a forest to form a sheet

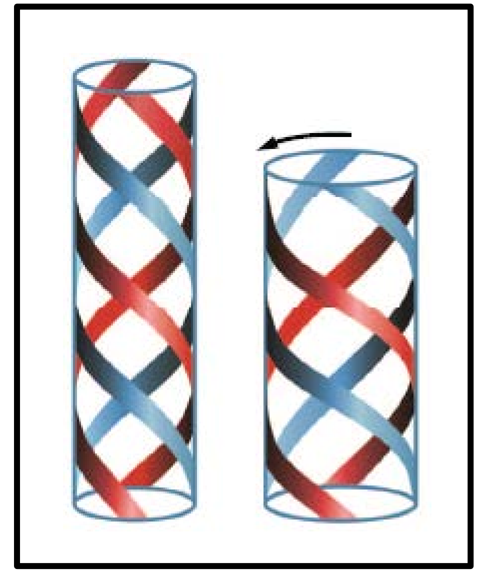
The measured gravimetric strength of orthogonally oriented sheet arrays exceeds that of sheets of high-strength steel.

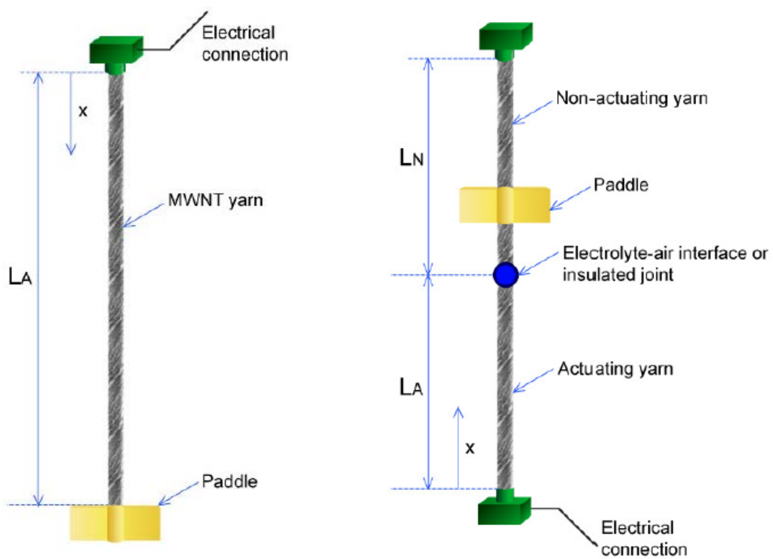
Science. **2005**, *309*, 1215.

Torsional CNT Artificial Muscles

Carbon nanotube yarn







Carbon nanotube yarn provides a reversible 15000 degree rotation and 590 revolutions per minute !!

Science. **2011**, *334*, 494.

Summary of Second Topic

1. ***Electroactive polymers appear to provide the best conbination of properties for muscle like actuation.***

2. ***The field of EAPs is under development.***

3. ***CNT artificial muscles show the best result.***

Today's Topics

1. *Basic concept and history of "Gel"*

2. *Application to artificial muscle*

3. *Future outlook*

Current Trends of Gel

Application of Gel

Medical field

Biochemistry

Biomaterial, DDS, Microallay etc…

Actuator

Functional gel

Strong Gel

TP gel, NC gel etc…

Analysis

Theory

Future Outlook

Gel with "emergence" functionality

Actin
Myosin
Interaction
Nano meter

→ ***Sarcomere***
Pico newton

→ ***Actual force***
Centi meter, kg

Gel has the potential to artificially mimic "biological emergence" !!

Future Outlook

Gel with "emergence" functionality

1. ***Artificial biological machine system***

Ex) muscle like gel engine, brain like computer, biomining…etc

2. ***Recognition of "life"***

Reference

1. 「驚異のソフトマテリアル　最新機能性ゲル研究」 日本化学会
2. 「ゲルハンドブック」 エヌティエス　長田義仁他
3. 「高分子ゲル」 高分子学会　吉田亮
4. 「図解　人工筋肉　ソフトアクチュエーターが拓く世界」 日刊工業新聞社　中村太郎

Appendix 1

Macromol. Rapid Commun. **2010**, *31*, 10.

Table 1. Comparison of actuator materials.

Type (specific)	Maximum strain	Maximum pressure	Specific elastic energy density	Elastic energy density	Coupling efficiency k^2	Maximum efficiency	Specific density	Relative speed (full cycle)	References
	%	MPa	$J \cdot g^{-1}$	$J \cdot cm^{-3}$	%	%			
Dielectric elastomer (acrylic with prestrain)	380	7.2	3.4	3.4	85	60–80	1	Medium	[2,3,164]
Dielectric elastomer (silicone with prestrain)	63	3	0.75	0.75	63	90	1	Fast	[164]
Dielectric elastomer (silicone – nominal prestrain)	32	1.36	0.22	0.2	54	90	1	Fast	[3]
Electrostrictive polymer [P(VDF–TrFE)]	4.3	43	0.49	0.92	–	≈80 (est.)	1.8	Fast	[3]
Electrostatic devices (integrated force array)	50	0.03	0.0015	0.0025	50 (est.)	>90	1	Fast	[3,4,164]
Electromagnetic (voice coil)	50	0.1	0.003	0.025	–	>90	8	Fast	[3,4]
Piezoelectric ceramic (PZT)	0.2	110	0.013	0.1	52	>90	7.7	Fast	[3]
Piezoelectric single crystal (PZT-PT)	1.7	131	0.13	1	81	>90	7.7	Fast	[3]
Piezoelectric polymer (PVDF)	0.1	4.8	0.0013	0.0024	7	–	1.8	Fast	[3]
Shape memory alloy (TiNi)	>5	>200	>15	>100	5	<10	6.5	Slow	[3]
Shape memory polymer (polyurethane)	100	4	2	2	–	<10	1	Slow	[3]
Thermal (expansion – Al, dT = 500 K)	1	78	0.15	0.4	–	<10	2.7	Slow	[3]
Conducting polymer (PANI)	10	450	23	23	<1	<5 (est.)	≈1	Slow	[3,4]
Ionic gels (polyelectrolyte)	>40	0.3	0.06	0.06	–	30	≈1	Slow	[3]
Magnetostrictive (terfenol-D)	0.2	70	0.0027	0.025	–	60	9	Fast	[3]
Natural muscle (human skeletal)	>40	0.35	0.07	0.07	–	>35	1	Medium	[3]
Natural muscle (peaks in nature)	100	0.8	0.04	0.04	–	40	–	Slow–fast	[2,4]

Appendix 2

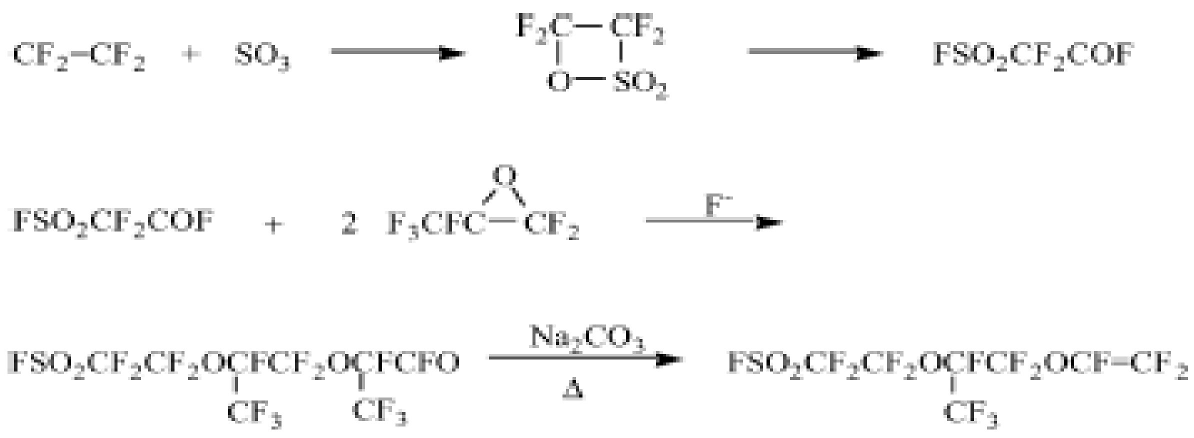
Preparation procedure for IPMCs

Supply: Nafion, $NaBH_4$, Aqueous solution of platinum ammine complex, Hydrazine hydrate
Hydroxylamine hydrochloride, Diluted ammonium hydroxide solution,
Diluted hydrochloric acid, Deionized water

1. **Surface roughening of the membrane**
   a. Mild sandblast
   b. Ultrasonic washing
   c. Treatment with HCl
   d. Treatment with water
2. **Ion-exchange**
3. **Primary plating**
4. **Secondary plating**

Appendix 3

Synthesis of comonomer



J. Fluorine. Chem. **2004**, *125*, 1211.