OF POLYMERS: ENDLESS POSSIBILITIES FOR INDUSTRIAL APPLICATIONS

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«Low Energy Electron Beams for Industrial and Environmental Applications» EuCARD-2 Workshop with Industry, 8-9 December 2016, Warsaw, Poland

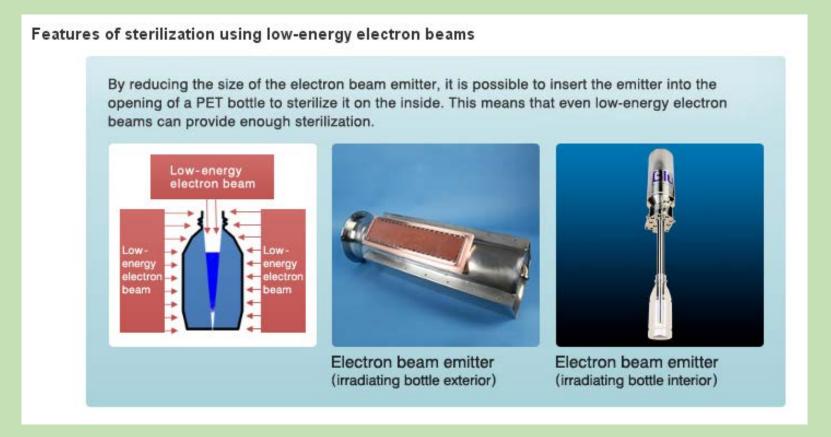
APPLICATIONS OF LOW ENERGY EB ACCELERATORS

- Industrial
- Energy
- Health-care
- Environmental
- Emergency

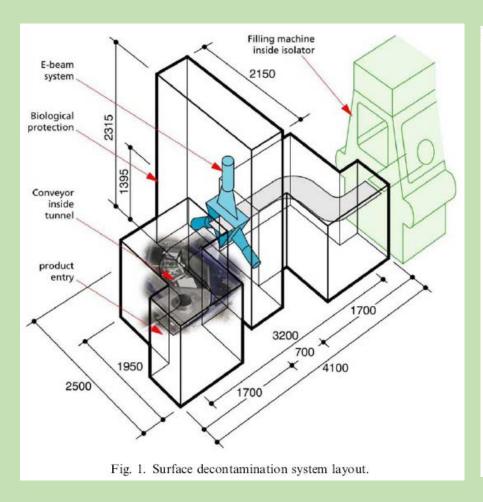
INDUSTRIAL APPLICATIONS

- Sterilization
- Decontamination
- Antibacterial packaging
- Pressure sensitive adhesives
- Surface modification
- Thin film crosslinking

LOW ENERGY EB STERILIZATION



SURFACE DECONTAMINATION IN PHARMACEUTICAL FILLING LINE





ENERGY CONVERSION & STORAGE

Progress in Polymer Science 63 (2016) 1-41



Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

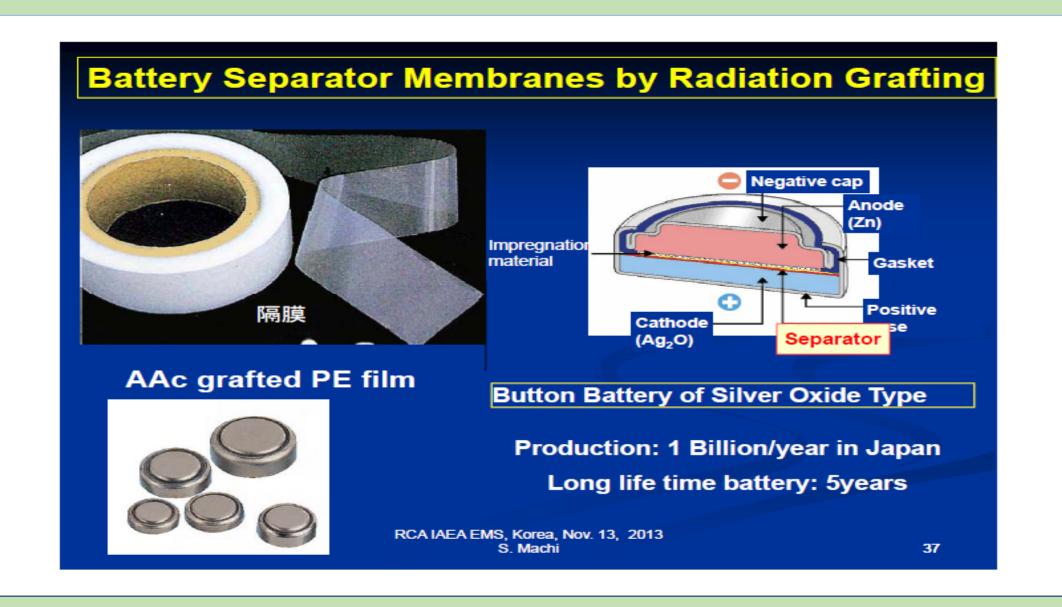


Radiation-grafted materials for energy conversion and energy storage applications



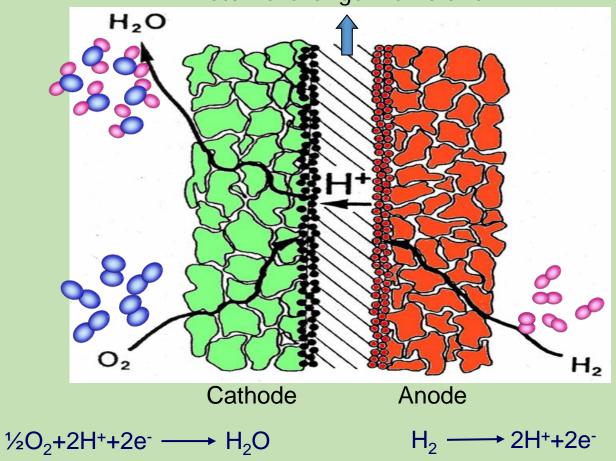
Mohamed Mahmoud Nasef^{a,b}, Selmiye Alkan Gürsel^{c,d}, Duygu Karabelli^e, Olgun Güven^{f,*}

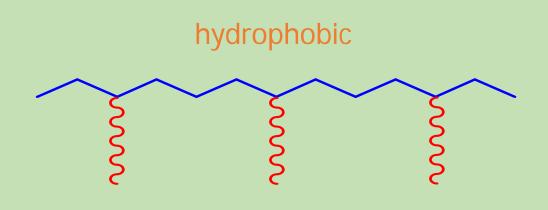
- ² Center of Hydrogen Energy, Institute of Future Energy, International Campus, Universiti Teknologi Malaysia, Jalan Semarak, 54000 Kuala Lumpur, Malaysia
- b Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia, Jalan Semarak, 54100 Kuala Lumpur, Malaysia
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Polymer-Electrolyte Membrane

Proton-exchange membrane





PSI Membrane Materials-Cost Estimation

Polymer	
25 mm thick FEP film:	1 m ²
Solvents	
Ethanol (wash film)	0.20 L
Isopropanol (grafting)	2.42 L
Toluene (wash grafted film)	0.50 L
Dichloromethane (sulfonation)	0.33 L
Water (grafting, washing)	20 L
Monomers	
Styrene	1.0 L
DVB	0.11 L
Acids/Bases	
Chlorosulfonic Acid	0.03 L
NaOH	0.03 kg
Sulfuric Acid (2 M)	8.33 L

Total estimated raw materials cost for 1 m² PSI Membrane:

 \sim USD 15 /m²

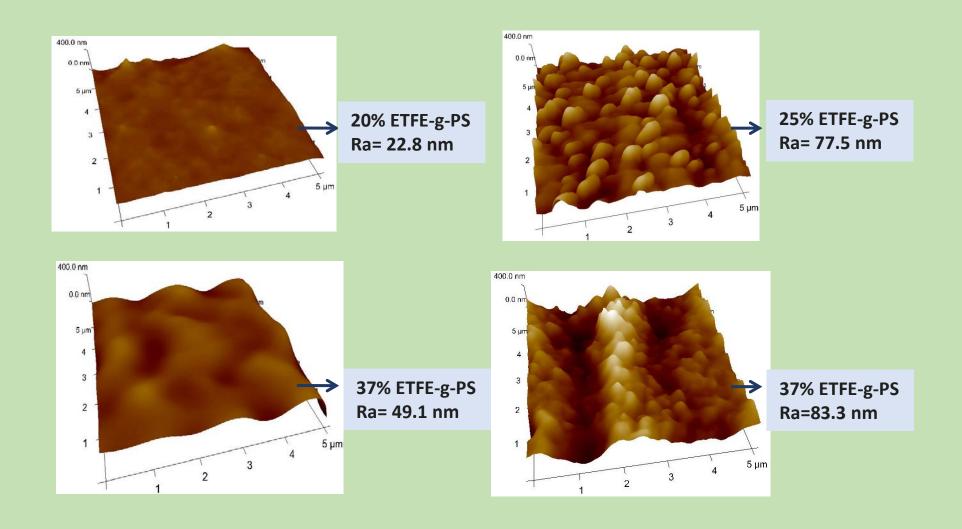
*PSI Membrane: ~ USD 3/ kW [1] *Nafion® Membrane: ~ USD 100/kW [2]

*assuming p=0.5 W/cm²

[1] L. Gubler, N. Prost, S. Alkan Gürsel, G. G. Scherer, *Solid State Ionics* 176, 2849 (2005)

[2] M. Doyle, G. Rajendran, *Handbook of Fuel Cells—Fundamentals, Technology and Applications*, Vol. 3, W. Vielstich, A. Lamm, H. Gasteiger, Editors. p. 351, John Wiley & Sons, Ltd, Chichester (2003)

RAFT-mediated Grafting for the Preparation of Fuel Cell Membranes



Fuel Cell membranes based on radiation –grafted ETFE

Graft Ratio, %	IEC	Water Uptake, %	Hydration Number, λ	Conductivity σ mS.cm ⁻¹	Reference
36	1,51	30	-	43	Kallio T. et al., 2002
45-55	2.15-2.45	-	11	70	Yosuke K. et al., 2008
51.7	2.22	14.2	3.55	41	Gubler L. et al. 2005
30.4	1.66	10.3	3.44	20	Gubler L. et al., 2005
37*	1.71	41	13	43	Our Work
48*	2.03	64	17	148.5	Our Work



Storage of Energy



Redox Flow Batteries

When solar or wind power is produced at the wrong time of the day we need to store it during the evening demand peaks.

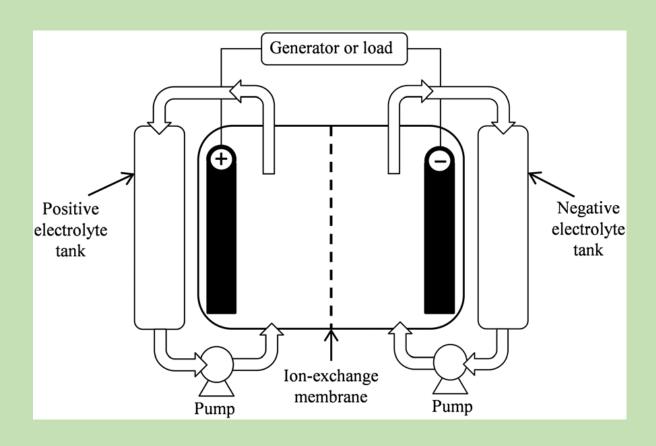
Redox flow batteries seem to be a good option.

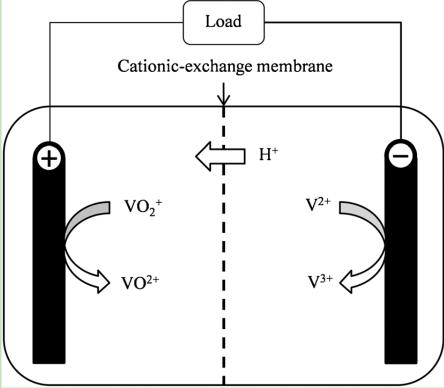
Vanadium is used in new flow batteries which can store large amounts of energy, perfect for remote wind or solar systems.

All-vanadium battery is the most widely commercialized RFB used for large-scale energy storage.

All-vanadium redox flow battery:

A dual electrolyte system, Redox couple separated by a cation-exchange membrane Minimum risk of cross-contamination





The Membrane

- The membrane is a key component in a vanadium redox flow battery system because it defines the performance and economic viability of the system.
- The time to first service of the VRB Power system is dependent on the life expectancy of the membrane, which was guaranteed for 10 years.

M. M. Nasef, S. A. Gürsel, D. Karabelli, Olgun Güven, «Radiation-grafted materials for energy conversion and energy storage applications», Prog. Polym. Scien., 63 (2016) 1-41

The Importance of Electrolyte

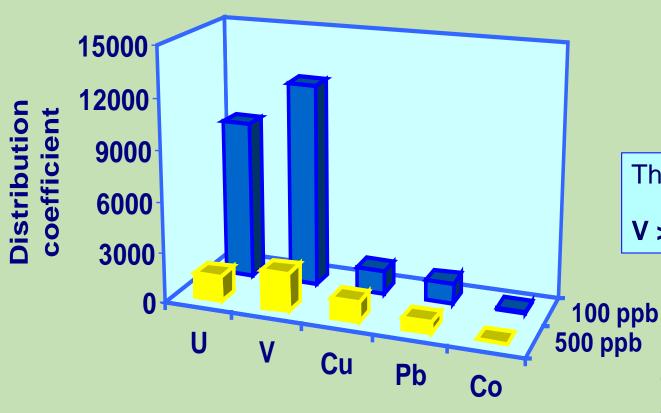
- The high cost of the electrolyte is one of the primary factors limiting the overall cost effectiveness of the vanadium battery.
- Both the manufacture of electrolyte from the dissolution of vanadium pentoxide (V₂O₅) in sulphuric acid and the optimisation of vanadyl sulphate (VOSO₄) solubility are non-trivial processes because the concentrations of the major species are dependent on the composition and temperature.
- A considerable number of vanadium-based electrolyte patents have been (or are still) active, and these tend to limit commercial applications without licence.

Solution: Recovery of vanadium from sea water

M.M. Nasef & O. Güven, Progress in Polymer Science, 37(2012)1597-1656

G. Kear, A. A. Shah, F.C. Walsh «Development of the all-vanadium redox flow battery for energy storage: a review of technological, financial and policy aspects», Int. J. Energy Res., 36 (2012) 1105–1120

RECOVERY OF URANIUM AND VANADIUM FROM SEAWATER



The selectivity expressed as the distribution coefficient (D)

The order of selectivity;

V > U >> Cu ≥ Pb >> Co

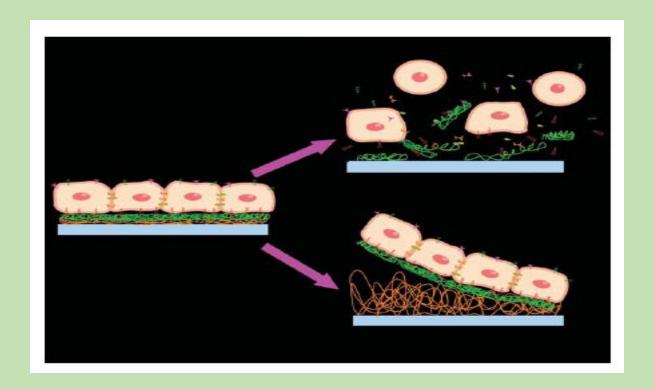
Adsorption selectivity of amidoximated nonwoven fabric for the indicated metal ions at two different initial concentrations

These results show that the new adsorbent is suitable for enrichment of trace amounts of U and V ions from seawater or other aqueous media.

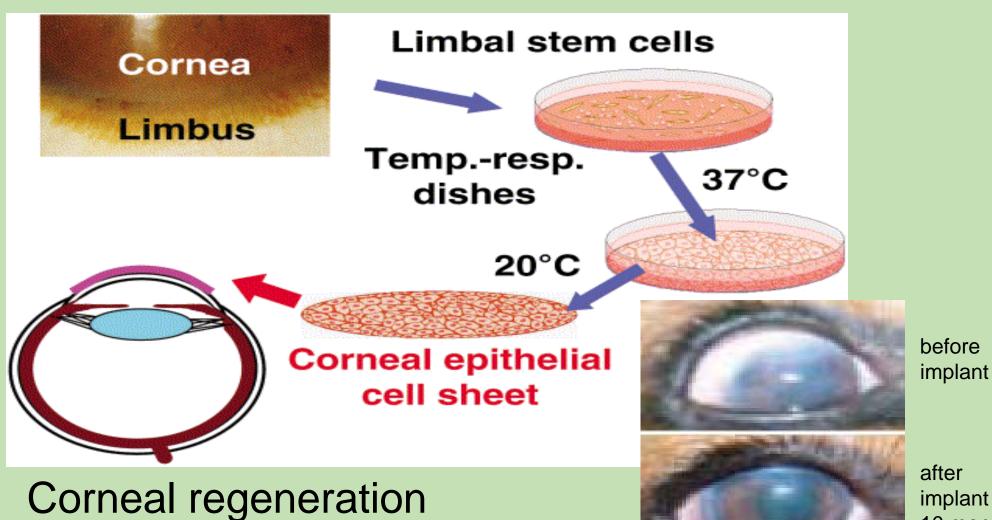
HEALTH-CARE APPLICATIONS

- Tissue Engineering
- Implants

CELL SHEET HARVEST



Scaffold-free tissue engineering

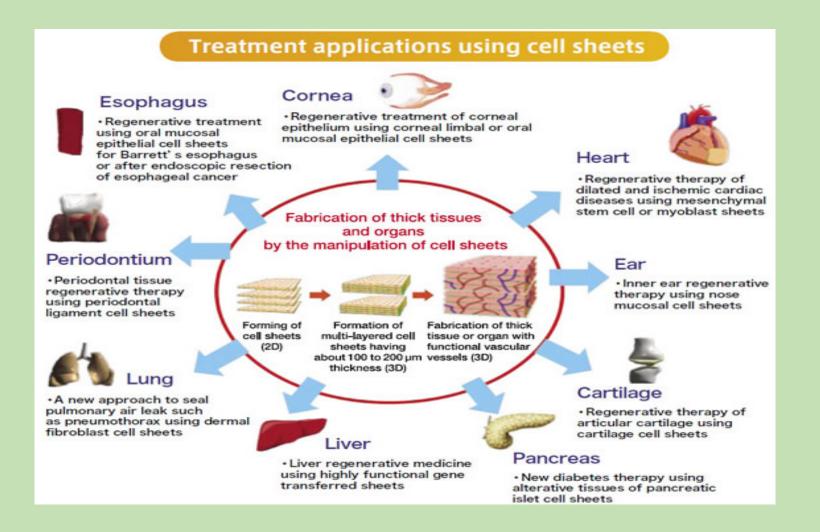


Yamato & Okano, 2004

after implant 10 months

Cell Seed Ltd.,

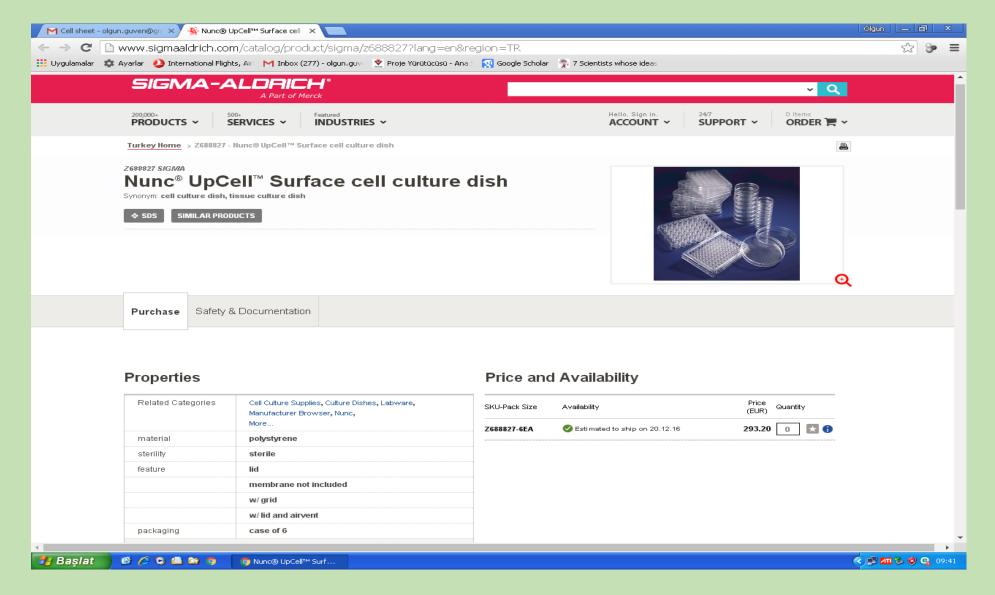
Applications of Cell Sheets



Impact of Cell Sheet Development

- Making the cell sheet from the person himself for regenerative medicine has succeeded without using serum of animal origin.
- ■ The process of detaching cell sheets without damage to the structure of the cell membrane by temperature changes (from 37°C to 20°C) has been successfully analyzed. The sheets can be applied in regeneration medicine because they are rapidly detached without damaging the structure and functions of the cell membrane.
- Platform technology for regeneration medicine targeting tissues such as skin, cardiac muscle, corneas, bladder, esophagus, lungs, blood vessels and liver has been successfully developed.
 Clinical application with the cornea and myocardium has commenced in Japan. Clinical testing with the cornea commenced in France for marketing authorization in 2011.

Cell Culture Dish



Cell Culture Dish

Description

General description

The Nunc UpCell Surface dishes have a temperature responsive cell culture surface. These UpCell Surface dishes are suitable for harvesting of cells with intact surface proteins, for culture passaging, single-cell analyses and cell transplantation research. The UpCell surface enables harvesting of cell sheets and creation of 3D tissue models which are held together by normal cell junctions and extracellular matrix.

- · Harvesting of cells with intact surface proteins
- No trypsinization preserve cell surface proteins
- · No physical force get high cell viability
- Releases adherent cells by reduction of temperature of the cell culture
- For culture passaging, single-cell analyses and cell transplantation research.
- Enables harvesting of cell sheets and creations of 3D tissue models held together by normal cell junctions and extracellular matrix
- · Minimal hands-on time
- · For research and single-use only
- It is quick, clean and simple-just reduce the temperature

Note: Suitable for the harvesting of cells with intact surface proteins, for cell culture passage, single-cell analyses and cell transplantation research

Legal Information

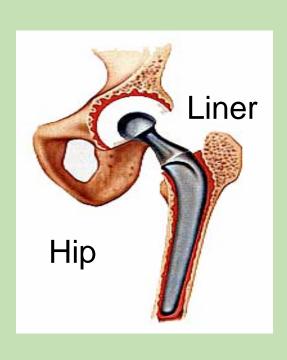
Nunc is a registered trademark of Thermo Fisher Scientific or its subsidiaries

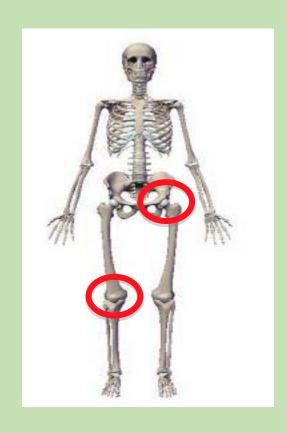
UpCell is a trademark of Thermo Fisher Scientific or its subsidiaries

IMPLANTS

UHMWPE artificial Joint

Radiation crosslinked ultra high molecular weight PE





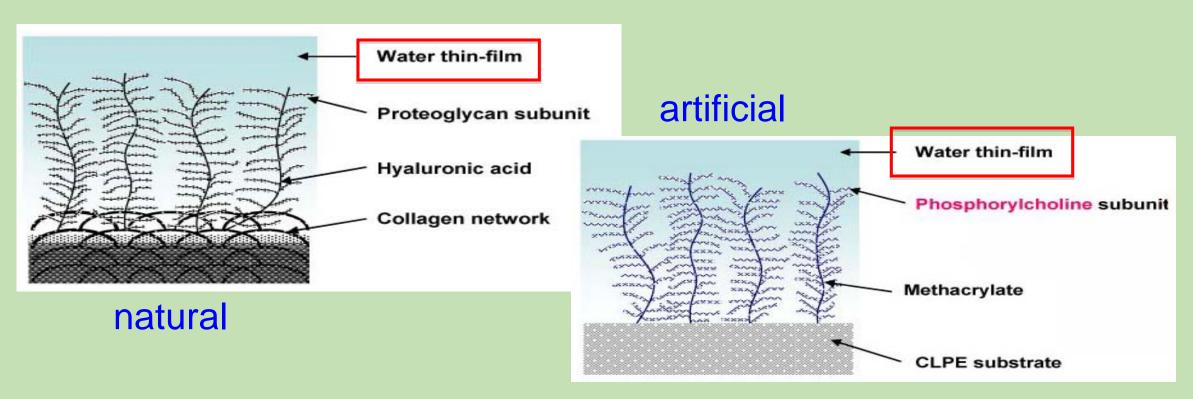


New approach to enhance wear resistance

surface modification of UHMWPE with synthetic cartilage by graft polymerization

Commercialized in 2011 by Kyocera Medical Corporation

Structures of natural and synthetic cartilage



Water thin film acts as extremely efficient lubricant



Contents lists available at SciVerse ScienceDirect

Biomaterials

journal homepage: www.elsevier.com/locate/biomaterials



Biomimetic hydration lubrication with various polyelectrolyte layers on cross-linked polyethylene orthopedic bearing materials

Masayuki Kyomoto ^{a,b,d}, Toru Moro ^{b,c}, Kenichi Saiga ^{a,b,d}, Masami Hashimoto ^e, Hideya Ito ^c, Hiroshi Kawaguchi ^c, Yoshio Takatori ^{b,c}, Kazuhiko Ishihara ^{a,*}

^{*}Department of Materials Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

b Division of Science for Joint Reconstruction, Graduate School of Medicine, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

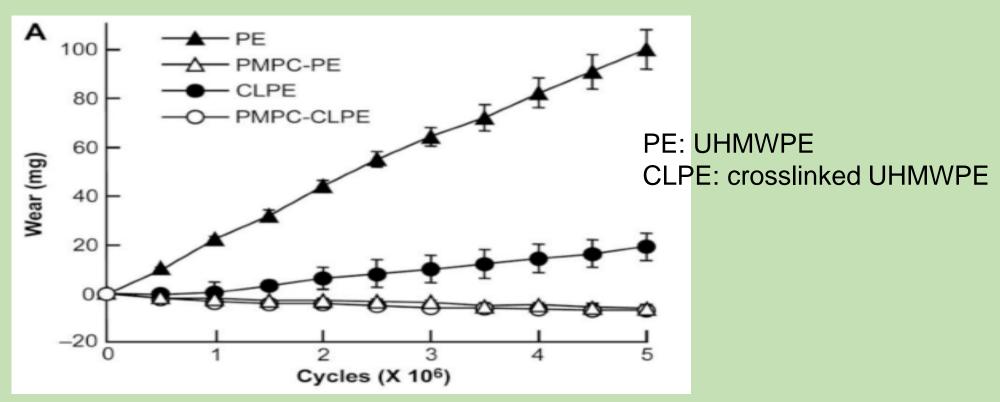
^cSensory & Motor System Medicine, Faculty of Medicine, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

d Research Department, Japan Medical Materials Corporation, 3-3-31 Miyahara, Yodogawa-ku, Osaka 532-0003, Japan

^e Materials Research and Development Laboratory, Japan Fine Ceramics Center, 2-4-1 Mutsuno, Atsuta-ku, Nagoya 456-8587, Japan

Wear resistance of PMPC

Excellent wear resistance without crosslinking



RADIATION GRAFTING OF SUTURES

POLYMER REVIEWS 2016, VOL. 56, NO. 4, 607–630 http://dx.doi.org/10.1080/15583724.2015.1119163



REVIEW

Antimicrobial Surgical Sutures: Recent Developments and Strategies

Mythili Tummalapalli, Sadiya Anjum, Shanti Kumari, and Bhuvanesh Gupta

Bioengineering Lab, Department of Textile Technology, Indian Institute of Technology, New Delhi, India

setting. Presently, very few antimicrobial surgical sutures are available commercially. Therefore, there is a great scope for market development in this area.

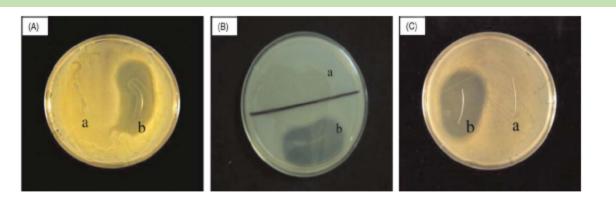


Figure 5. Antimicrobial activity of PP-g-PAN/TCH monofilaments against (A) S.aureus, (B) E.coli and (C) K. pneumonia.⁵⁰ © John Wiley and Sons. Reproduced by permission of John Wiley and Sons. Permission to

Environmental Applications of Radiation- Grafted Polymers

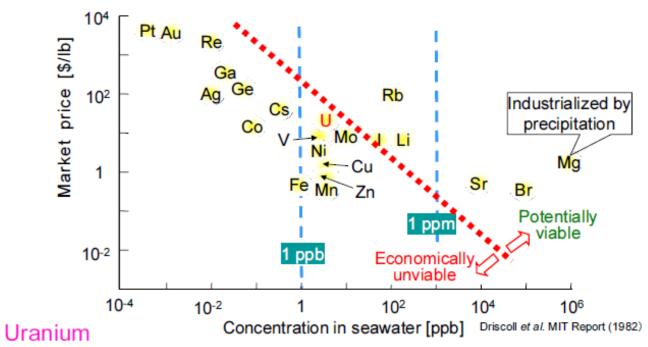
- Desalination
- Ultrapure water production
- Recovery of precious metals
- Recovery of uranium from seawater
- Removal of heavy metals from industrial ww
- Removal of toxic gases

[&]quot;Radiation-grafted copolymers for separation and purification purposes: Status, challenges and future directions"

M.M. Nasef & O. Güven, Progress in Polymer Science, 37(2012)1597-1656

Mineral resources in Seawater

Cost-effectiveness of minerals in seawater



- 3.3 ppb in seawater
- near boundary of costeffectiveness

Commercialization of uranium collection from seawater:

How do we develop a cost-effective methods?

A comparison of uranyl ion adsorption using various amidoximated polymeric adsorbents

Research groups	Adsorbent [*]	Uranyl ions adsorbed	Uranyl ions adsorbed normalized to 20 L of total working volume
Güven et al. (2007) A	GMA grafted polypropylene/ polyethylene nonwoven fabrics modified with 3,3'-iminodipropionitrile	0.005 mg/g U 0.0052 mg/g V	2.5 mg/g U 2.6 mg/g V
Egawa ^b et al. (1991)	Lightly crosslinked poly(acrylonitrile-co-divinylbenzene)	650 μg/g U	0.65 mg/g
Suzuki ^c et al. (2000)	Polypropylene nonwoven fabric grafted with acrylonitrile and methacrylic acid	0.576 mg/g U 1.8 mg/g V	0.576 mg/g U 1.8 mg/g V
Kawai ^d et al. (2000)	Polypropylene fabric cografted with methacrylic acid and acryloylchloride	0.2 mg/g U,	0.2 mg/g
Kise ^e et al. (1985)	Dicyanoethylated polystyrene	0.004 mg/g U	0.08 mg/g
Omichi ^f et al. (1986)	Acrylonitrile grafted onto tetrafluoroethylene-ethylene copolymer	0.2 mg/g U	0.08 mg/g
Kabay ^g et al. (1993)	Polypropylene fiber grafted with acrylonitrile	0.152 mg/g U	0.608 mg/g
Takedah et al. (1991)	Acrylonitrile grafted onto porous polyethylene hollow fiber	0.97 mg/g U	0.97 mg/g
Saito ⁱ et al. (1990)	Acrylonitrile grafted onto porous polyethylene hollow fiber	0.85 mg/g U	0.34 mg/g
Omichi ^j et al. (1985)	Fibrous adsorbent containing acrylic acid and acrylonitrile	0.04 mg/g U	0.08 mg/g

^{*} All PAN containing polymers or copolymers are amidoximated

^a Batch process from 3.3 ppb metal ion mixture solution, volume: 40 mL, the density of amidoxime group (AOD): 2 mmol/g, contact time: 24 h

^b 0.5 g resin, flow rate: 900 mL/h, seawater volume: 20 L, contact time: 10 days.

^c 0.07 g amidoxime fiber, the analysis was carried out for amidoxime fiber, which had been immersed in seawater for 30 days. AOD: 6.3 mmol/g

d 0.5 g resin, flow rate: 0.47 mL/h, seawater volume: 20 L, contact time: 24 hours. AOD: 3 mmol/g,

e 0.1 g resin, seawater volume: 1L, contact time: 96 h,

^f Semibatch process (5 L of seawater was intermittently exchanged with fresh seawater), total volume: 50 L, contact time: 10 days,

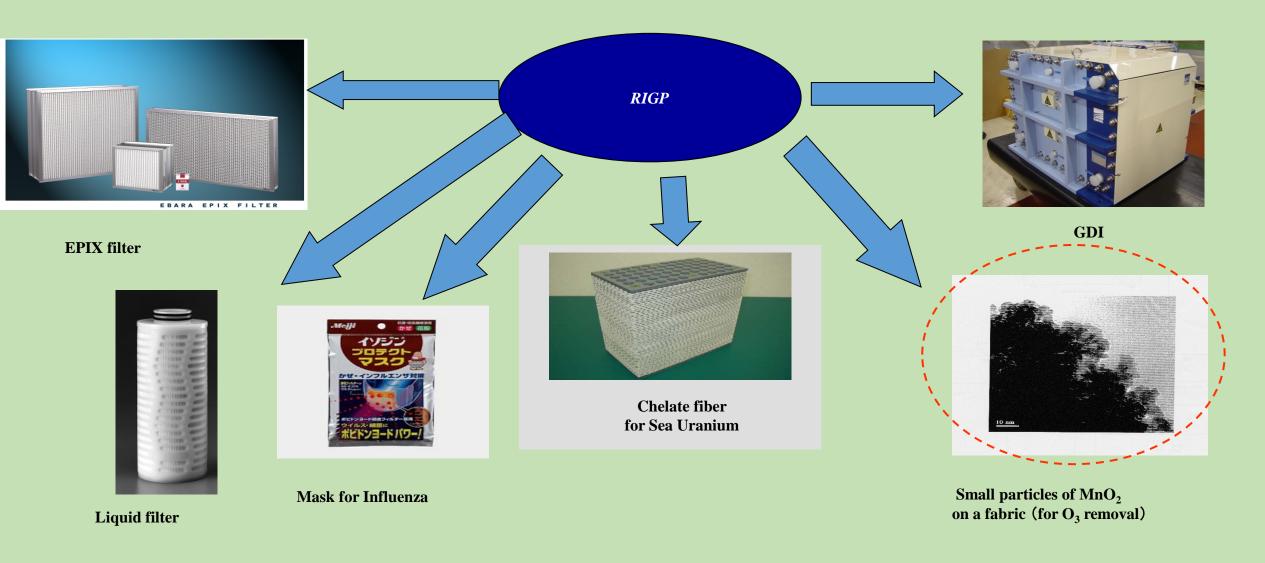
g Batch process, seawater volume: 5L, contact time: 24 h,

h A continuous-flow experiment, a bundle of 230 AO-H fibers, Contact time: 30 days, AOD: 11.3 mmol/g,

i 0.07 g amidoxime membrane, 1 L of seawater was intermittently exchanged with fresh seawater, total volume: 50 L, contact time: 50 days,

¹0.1 g resin, semibatch process (2 L of seawater was intermittently exchanged with fresh seawater), total volume: 10 L, contact time: 5 days

Application of grafted materials manufactured by EBARA



RIG ION EXCHANGE MEMBRANES

M.M. Nasef et al. / Progress in Polymer Science 63 (2016) 1-41

Table 2
List of commercial radiation-grafted ion-exchange membranes.

6

Company	Commercial name	Product	Origin
United technology	-	Fibrous ion-exchange sheets	Japan
Ebara Research Co., Ltd.	-	Sulfonic acid non-woven fabric Ion-exchange fabrics and ion conductive spacer	Japan
Pall Gellman Sci. Inc.	PERMION	Sulfonated polystyrene/PTFE	USA
RAI Research Corp.	R4010, R1010, and R4035	Cation-exchange membranes	
Solvay	R5010	Styrene/PE	USA
	CRA	Cation-exchange membrane	Belgium
	Morgan CDS	Cation-exchange membrane	
	Morgan ADP 100-2	Anion-exchange membrane	
Ashahi Glass Inc.	Flemion	Cation-exchange membrane	Japan
Shanghai Shilong	_	Sulfonic acid non-woven fabric	China
Hi-Techn. Corp. Ltd., CEC, Japan	RAYMION	Sulfonated polytrifluorostyrene/ETFE	Japan

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Review

Radiation-grafted copolymers for separation and purification purposes: Status, challenges and future directions

Mohamed Mahmoud Nasefa,b,*, Olgun Güvenc

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- b Malaysia japan International institute of Technology, International Campus, Universiti Teknologi Malaysia, Jalan Semarak, 54000 Kuala Lumpur, Malaysia
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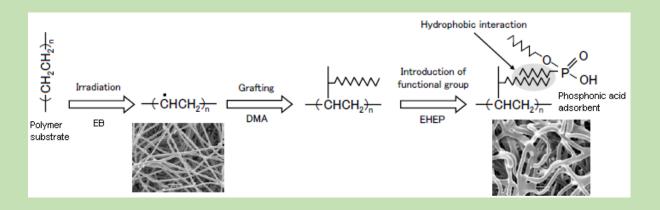
Keywords:

Radiation induced graft copolymerization Ion exchangers Chelating and affinity polymers Hydrogels Separation applications

ABSTRACT

Functional copolymers obtained by modification of existing polymers using radiation induced graft copolymerization are attractive materials due to their enhanced separation properties. For further progress, however, copolymers with favorable properties and geometries must be developed to address the growing demands in the field of separation and purification. In this review, the current status of research on the development and applications of radiation-grafted copolymers for separation and purification purposes is presented without neglecting the seminal work that laid the foundation to today's progress. The basic principles of this field including classifications and description of radiationgrafted copolymers with their engineering configurations and operating systems are reviewed. A wide range of diverse separation applications is addressed, covering water production, chemical industry, environmental remediation, biotechnology and biomedicine categories. The emerging applications of the new radiation-grafted materials (membranes, brushes, nanogels and microgels, hydrogels, fibers and monoliths) in separation technology are taken into account. The challenges hindering the utilization of radiation-grafted copolymers to wider commercialization applications are discussed. Future directions in developing and promoting new and advanced radiation-grafted copolymers to address separation challenges and move to new technological fronts are also deliberated.

RECOVERY OF SCANDIUM FROM HOT SPRINGS

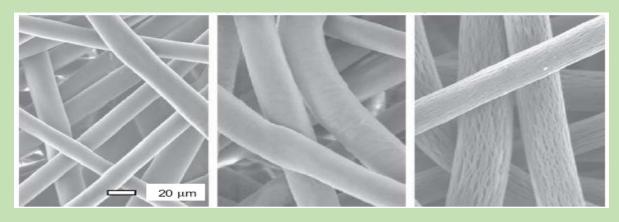


Scheme of preparation of Sc adsorbent by RIG



Pilot plant for recovery of Sc from hot springs Kusatu twon, Gunma prefecture, Japan

SPECIALTY ADSORBENTS



Radiation-induced grafting



1,2,4 triazole modified GMA grafted nonwoven fabric

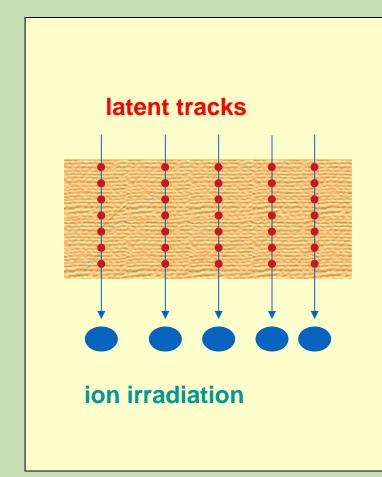


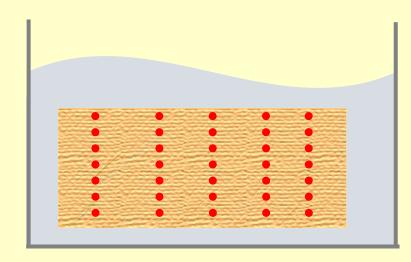
After Cu(II) ion loading



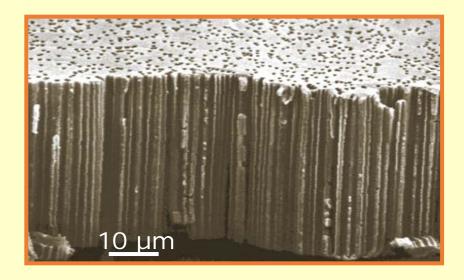
After Cr(VI) ion adsorption

Ion-Track Formation and Etching



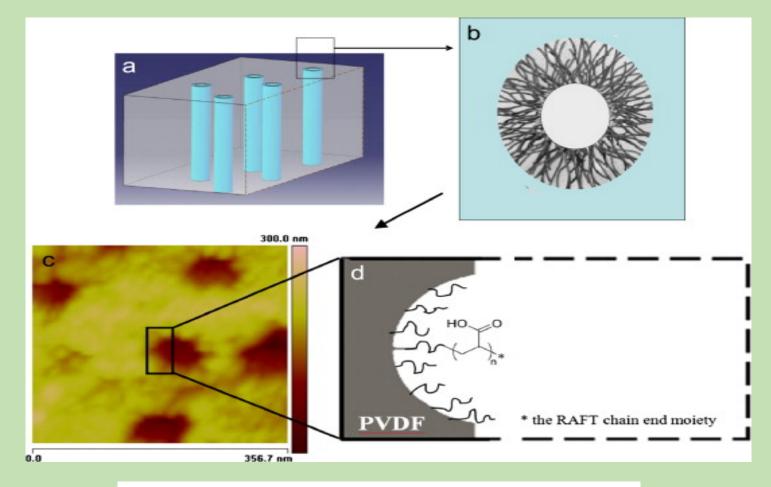


e.g. NaOH, NaOCI, HF



polymer track membrane

Functionalized Track-etched Membranes



M. Barsbay et al. / Journal of Membrane Science 445 (2013) 135-145

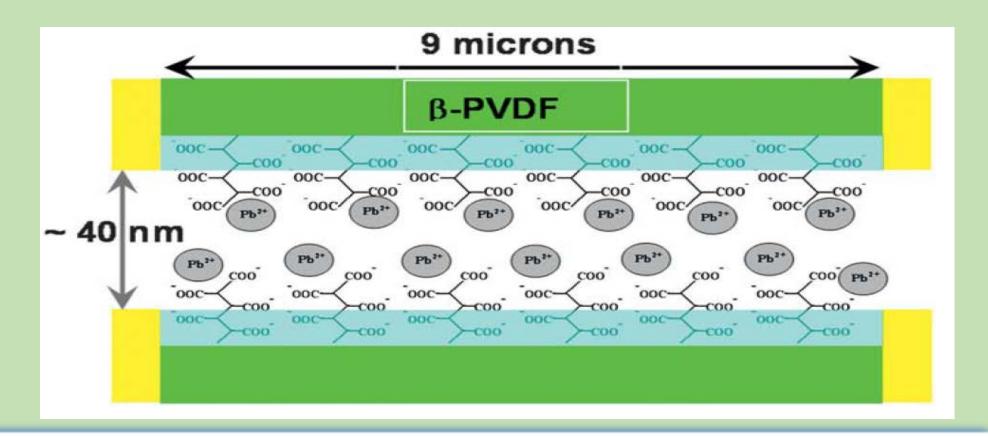
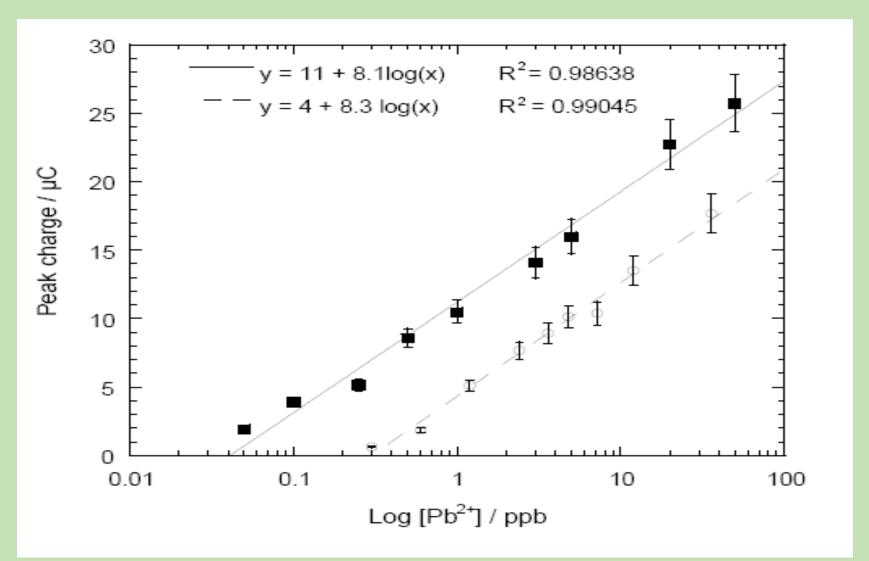


Diagram of a single nanopore from a gold coated 9 micron thick PAA grafted track etched b-PVDF membrane (FME) after absorbing Pb²⁺ ions from polluted water. The b-PVDF membrane is shown as green and the RCOO-as blue zones represents the PAA that is radio grafted into the 40 nm diameter nanopores of the membrane. The 35–40 nm thick gold coating is shown as yellow. The grey balls represent absorbed Pb²⁺ ions.



Calibration curve for Pb²⁺ ions determined from the peak charges for (**a**) RAFT polymerization and (o) conventional method.

European Patent 2011DI0057

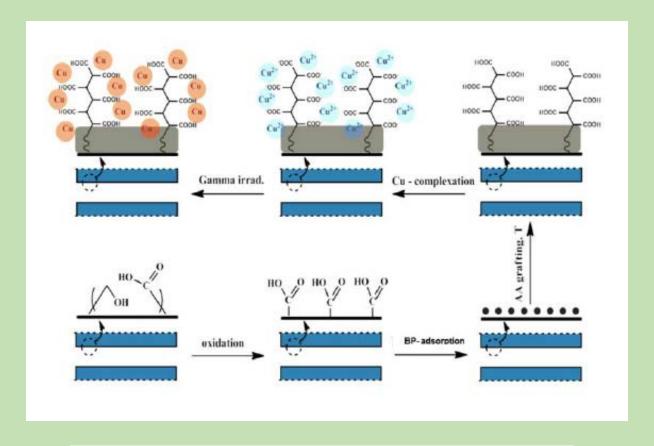
FIELD TESTS

H. Bessbousse et al. / Radiat

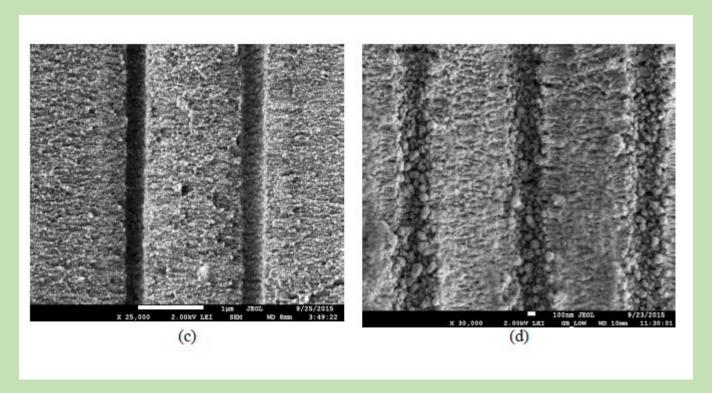


Fig. 1. Prototype photograph directly immersed in a natural water.

Scheme of Functionalization of Nanopores of PET TeMs







SEM microphotographs of cross-sectional view of PAA-g-PET TeMs (c), and PET TeMs with Cu nanoparticles (d) after γ-irradiation to a dose 98 kGy.

Preliminary tests proved successful as catalysts and sensors.

EMERGENCY APPLICATIONS

- Outbreak of H1N1
- Fukushima-Daichi Accident

Face Masks for H1N1

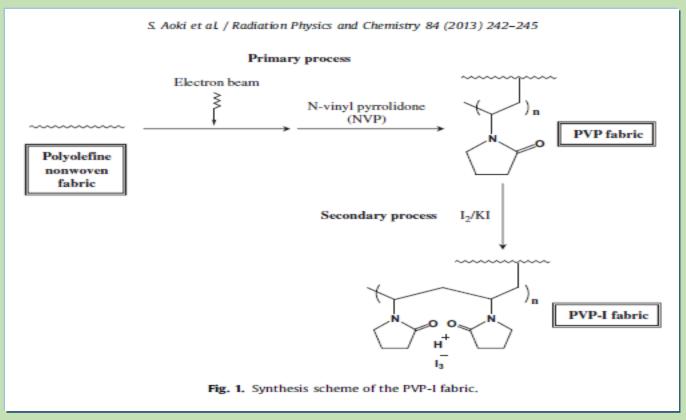
Upon outbreak of H1N1 flu in 2009, antibacterial fabric of 130000 m² was needed 133000 m² was shipped in six months



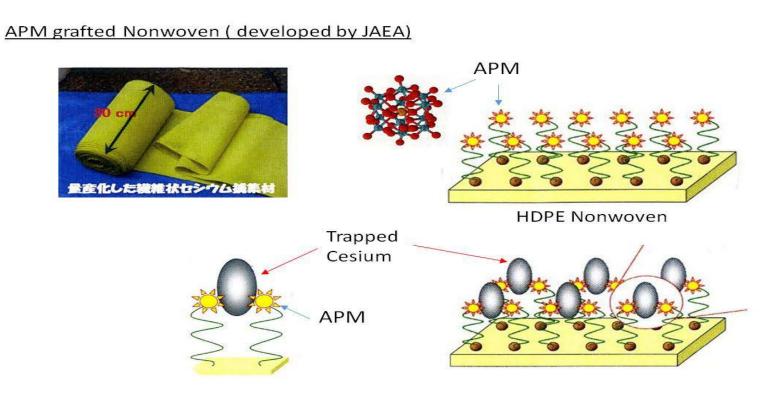
Conditions	of	continuous	RIGP	apparatus	on	NVP
grafting.						

Radiation source	Electron beam		
Total dose	< 160 kGy		
Atm osphere	Nitrogen		
Impregnated solution	NVP 30 wt% aqueous		
Fabric width	1500 mm		
Reaction mode	Continuous		
Temperature	< 337 K		





Fukushima-Daichi Accident Cs Removal



Development of Adsorbents for Cs Removal

Adsorption Performance Test

Filtration test on APM-grafted Nonwoven

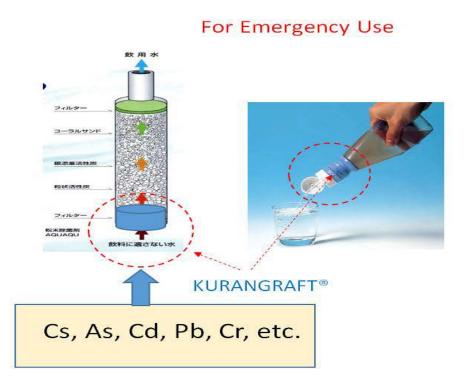
	Concentration (Bq/L)
Cesium Ion in Well-Water	88.0
Test-1 Batch test	N.D < (10)
Test-2 Column mode test	N.D < (10)

This data were released by Inner cabinet of Japan (11 Sep.2012) URL: http://www.go.jp/earthquake/nuclear/20120911_01.html

Cs Removal

Straw Type Aqua Filter





Chapter 15

ESTABLISHED AND EMERGING APPLICATIONS OF RADIATION-INDUCED GRAFT POLYMERIZATION

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Department of Chemistry, Hacettepe University, Beytepe, 06800, Ankara, Turkey

1. INTRODUCTION

Among various physical and chemical methods, radiation-induced graft polymerization (RIGP) has advantages over the other grafting techniques. Radiation-induced grafting is a means of modifying base polymers wherein grafts can result in a combination of properites related both to the base polymer backbone and to the grafted chains. Through the proper choice of monomers with appropriate functionalities, new properties such as biocompatibility, hydrophilicity, hydrophobicity, adhesion, friction resistance, barrier properties, etc. can be incorporated onto the radiation-activated polymers, especially very inert ones, as fluoropolymers, by graft copolymerization.



Ionizing Radiation: A Versatile Tool for Nanostructuring of Polymers

Journal:	Pure and Applied Chemistry
Manuscript ID	Draft
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Ionizing radiation: A versatile tool for nanostructuring of polymers

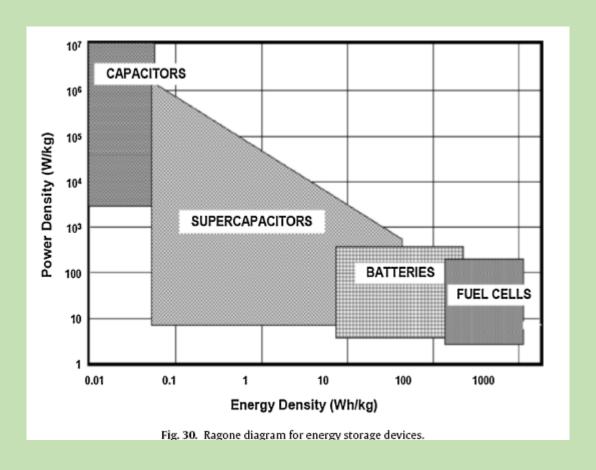
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Abstract:

Very high energies of particulate (accelerated electrons, swift heavy ions) or electromagnetic wave (gamma-, X-rays) radiation can be used to initiate free radical based reactions in solids, liquids or gases. Because of non-selectivity of absorption of ionizing radiation in matter free radicals are generated homogeneously in the bulk material. These free radicals on the polymers or monomers are used extensively in the synthesis and modification of polymeric materials. The unique properties of ionizing radiation make it a very useful tool in the top-down and bottom-up synthesis of nanomaterials. In this article the utilization of ionizing radiation in the form of swift heavy ions, accelerated electrons, X- and gamma rays will be described for development of advanced materials by radiation-induced grafting in nanoscale, synthesis of polymeric nanoparticles, radiation-assisted synthesis of nanogels and nanocomposites. The properties difficult to be attained by other techniques will be decribed by giving examples for the cases of ion track-etched membranes, fuel cell membranes, sensors, detectors, cell culture media, polymer thin films embedded with metal nanoparticles, polymer/clay nanocomposites with a prospect for the future outlook.

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Re-Emerging Field of Lignocellulosic Fiber – Polymer Composites and Ionizing Radiation Technology in their Formulation

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