Department of Chemistry for Materials

* nonmember

Composite Polymer Electrolytes Based on Poly(ethylene oxide), Hyperbranched Polymer, $BaTiO_3$ and $LiN(CF_3SO_2)_2$, Takahito ITOH, Yoshiaki ICHIKAWA, Takahiro UNO, Masataka KUBO, and Osamu YAMAMOTO*: Solid State Ionics, 156, pp. 393-399, 2003.

Composite polymer electrolytes based on poly(ethylene oxide) (PEO) with hyperbranched polymer (poly[bis(triethylene glycol)benzoate] capped with an acetyl group) (HBP), ceramic filler ($BaTiO_3$), and lithium salt ($LiN(CF_3SO_2)_2$) were examined as the electrolyte for all solid-state lithium polymer batteries and optimized to achieve high ionic conductivity. The ionic conductivity of the optimized composite polymer electrolyte, $[(PEO-20\ wt.\%\ HBP)_{12}(LiN(CF_3SO_2)_2)]-10\ wt.\%\ BaTiO_3$, where the PEO with number-average molecular weights (M_n) of 60×10^4, HBP with M_n of 15,000 and $BaTiO_3$ with a particle size of 0.5 μm were used, was found to be 2.6×10^{-4} S/cm at 30 ºC and 5.2×10^{-3} S/cm at 80 ºC, respectively. The optimized composite polymer electrolyte showed an electrochemical stability window of 4.0 V and was stable until 312 ºC under air.

Spontaneous Polymerization Mechanism of Electron-Accepting Substituted Quinodimethane with *p*-Methoxystyrene, Yukihiro MITSUDA, Takashige FUJIKAWA, Takahiro UNO, Masataka KUBO, and Takahito ITOH: Macromolecules, 36, pp. 1028-1033, 2003.

Spontaneous reactions of 1-(2,2-dimethyl-1,3-dioxane-4,6-dione-5-ylidene)-4-(dicyanomethylene)-2,5-cyclohexadiene (QM1) with *p*-methoxystyrene (MeOSt) were investigated in chloroform at room temperature at different monomer feed ratios. The hexane-insoluble products were to be copolymers of 7-(4-methoxyphenyl)-8,8-dicyanoquinodimethane (QM2) with small amounts (3-6 mol%) of the QM1, and the reaction product in the hexane-soluble fractions was to be the one-to-one adduct (Cycloadduct) of methylene Meldrum's acid (MM) with MeOSt. It was found that in the spontaneous reaction of the QM1 with MeOSt a side reaction involving a metathesis process took place to form new two products, QM2 and MM, and the former polymerized and the latter underwent the cycloaddition reaction with MeOSt.

Composite Polymer Electrolytes of Poly(ethylene oxide)/$BaTiO_3$/Li Salt with Hyperbranched Polymer, Takahito ITOH, Yuko MIYAMURA, Yoshiaki ICHIKAWA, Takahiro UNO, Masataka KUBO, and Osamu YAMAMOTO*: Journal of Power Sources, 119-121, pp. 403-408, 2003.

Composite polymer electrolytes composed of poly(ethylene oxide) (PEO), $BaTiO_3$ as a ceramic filler, $LiN(CF_3CF_2SO_2)_2$ as a lithium salt, and hyperbranched polymer (HBP) (poly[bis(triethylene glycol)benzoate] capped with an acetyl group) as a plasticizer were examined as the electrolyte for all solid-state lithium polymer batteries and the ionic conductivity was optimized. The optimized 90 wt.% $[(80\ wt.\%\ PEO-20\ wt.\%\ HBP)_{12}(LiN(CF_3CF_2SO_2)_2)]-10\ wt.\%\ BaTiO_3$ electrolyte, where the PEO with M_n of 60×10^4, HBP with M_n of 15,000 and $BaTiO_3$ with a particle size of 0.5 μm were used, showed the ionic conductivity of 1.3×10^{-4} S/cm at 30 ºC and 1.6×10^{-3} S/cm at 80 ºC, respectively. The optimized composite polymer electrolyte has an electrochemical stability window of 4.0 V and also it was stable until 307 ºC under air.

Effect of "Topotactic" Reduction Product of Molybdenum Disulfide on Catalytic Activity of Metallocene Catalyst for Olefin Polymerization, Satoru YAMADA, Akihiro YANO*, Morihiko SATO*, and Takahito ITOH: Journal of Molecular Catalysis A: Chemical, 200, pp. 239-349, 2003.

N,*N*-Dimethylanilinium salt of molybdenum disulfide (MoS_2) was developed as a novel cocatalyst for metallocene catalysts. The cocatalyst is composed of *N*,*N*-dimethylanilinium ion as a cationic part and "topotactic" reduction product of MoS_2, obtained by acquisition of an electron by neutral host lattice of MoS_2 without structural alteration, as an anionic part. In ethylene polymerization, addition of the *N*,*N*-dimethylanilinium salt of MoS_2 to the bis(indenyl)zirconium dichloride (Ind_2ZrCl_2)/triethylaluminum (Et_3Al) catalyst improved a catalytic activity per mmol of Ind_2ZrCl_2. The catalytic activity for this catalyst system activated by addition of the cocatalyst depended significantly on the amount of the cocatalyst and the *N*,*N*-dimethylanilinium ion content in the cocatalyst.

Synthesis and Polymerization of Novel Quinone Methide Ketals, Ayako SENO, Takahiro UNO, Masataka KUBO, and Takahito ITOH: Polymer Bulletin, 50, pp. 1-8, 2003.

Novel quinone methide ketals, 8-[1'-cyano-1'-(ethoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]deca-6,9-diene (**1a**) and 8-(1',1'-dicyanomethylene)-1,4-dioxaspiro[4.5]deca-6,9-diene (**1b**), were synthesized, and their polymerization behavior was investigated. Polymerizations of **1a** and **1b** initiated with BPO and $BF_3 \cdot Et_2O$ gave corresponding novel ring-opening polymers, but no polymerization with BuLi. Copolymerization of **1a** with St in the presence of AIBN at 60 ºC gave the monomer reactivity ratios $r_1(1a) = 0.50 \pm 0.1$ and $r_2(St) = 0.1 \pm 0.02$, and Q and e values of **1a** were 2.46 and +0.93, indicating that **1a** is a highly conjugative, electron-accepting monomer. Homopolymers of **1a** and **1b** had better thermal stability than that of 7-cyano-7-(ethoxycarbonyl)-1,4-benzoquinone methide.

Thermal, Electrical, and Mechanical Properties of Composite Polymer Electrolytes Based on Cross-Linked Poly(ethylene oxide-co-propylene oxide) and Ceramic Filler, Zhaoyin WEN, Takahito ITOH, Takahiro UNO, Masataka KUBO, and Osamu YAMAMOTO*: Solid State Ionics, 160, pp. 141-148, 2003.

A fully amorphous cross-linked poly(ethylene oxide-*co*-propylene oxide) (poly(EO/PO)) polymer electrolyte was prepared by chemical cross-linking reaction of a macro-monomer, poly(ethylene oxide-*co*-propylene oxide) with trifunctional cross-linkable acryloyl groups at the macro-monomer chain end. The lithium salt $LiN(CF_3SO_2)_2$ ([Li]/[O]=1/16) and ceramic fillers such as $BaTiO_3$ and γ-$LiAlO_2$ adopted in the polymer electrolyte could maintain the fully amorphous feature of the polymer matrix. The sub-micron and nano-sized $BaTiO_3$ fillers slightly decreased the thermal decomposition temperature of the polymer matrix, while the nano-sized γ-$LiAlO_2$ filler improved to some extent the thermal stability of the polymer matrix.

An Investigation of Poly(ethylene oxide)/saponite-based Composite Electrolytes, Zhaoyin WEN*, Zhonghua GU*, Takahito ITOH, Zuxiang LIN*, and Osamu YAMAMOTO*: Journal of Power Sources, 119-121, pp. 427-431, 2003.

Two kinds of composite, based on poly(ethylene oxide) (PEO) and a mineral saponite, were prepared and their thermal behavior, phase composition, microstructure and electrical properties were investigated. The results showed that PEO easily intercalates to the interlayer of saponite, replaces the interlayer water molecules, and acts as medium for lithium ion conduction. PEO-intercalated saponite exhibited conductivity as high as 4.1×10^{-3} S cm^{-1}, a lithium ion transference number of 0.99 at 25 ºC and conductivity activation energy of 0.14 eV. Appropriate amounts of intercalated PEO in the interlayer of saponite is important to an ideal ionic conductivity. The PEO-intercalated saponite is thermally stable below 350 ºC. In addition, a PEO-based composite with lithium saponite as filler showed homogeneous morphology and combined properties of individual PEO and saponite.

Polymerization by Insertion of Molecular Oxygen into Crystals of 7,7,8,8-Tetrakis(ethoxy-carbonyl) quinodimethane, Shinji NOMURA, Takahito ITOH, Masaki OHTAKE, Takahiro UNO, Masataka KUBO, Atsushi KAJIWARA*, Kazuki SADA*, and Mikiji MIYATA*: Angewandte Chemie International Edition, 42, pp. 5468-5472, 2003.

7,7,8,8-Tetrakis(ethoxycarbonyl)quinodimethane (**1**) copolymerized with oxygen in the solid state to give a highly crystalline alternating copolymer via a radical mechanism, but in vacuo no thermal and photo solid-state polymerizations of **1** took place. X-ray crystallographic study explained well that unique arrangement of **1** in the crystalline state provides copolymerization with molecular oxygen.

Cyclic Polyelectrolyte: Synthesis of Cyclic Poly(acrylic acid) and Cyclic Potassium Polyacrylate, Masataka KUBO, Takeshi NISHIGAWA, Takahiro UNO, Takahito ITOH, and Hiroaki Sato*: Macromolecules, 36, pp. 9264-9266, 2003.

α-Amino, ω-carboxyl heterodifunctional poly(*tert*-butyl acrylate) was prepared by a living anionic polymerization of *tert*-butyl acrylate using 1-phenyl-1-[4-(2,2,5,5-tetramethyl[1,2,5]azadisilolidinyl) phenyl]hexyl lithium and succinic anhydride as an initiator and terminator, respectively. Its intramolecular cyclization was carried out to obtain cyclic poly(*tert*-butyl acrylate) which was converted to cyclic poly(acrylic acid) and potassium polyacrylate

Surfactant Properties of Purified Polyglycerol Monolaurates, Tomoharu KATO*, Takashi NAKAMURA*, Masatsugu YAMASHITA*, Masami KAWAGUCHI, Tadaya KATO, and Takahito ITOH: Journal of Surfactants and Detergents, 6, pp. 331-337, 2003.

A series of purified polyglycerol monolaurates (PGML), such as di-, tri-, tetra, and pentaglycerol monolaurates, were synthesized, and their surfactant properties in aqueous solutions were examined. The surfactant properties of PGML were compared with those of *n*-dodecyl polyoxyethylene monoethers ($C_{12}EO_n$) to examine the function of the hydrophilic part of these compounds. The critical micelle concentration (CMC) values and the surface tension at CMC of PGML and $C_{12}EO_n$ increased linearly with an increase in the number of glycerol and oxyethylene units, respectively; the slope of the increase was greater for PGML than $C_{12}EO_n$. The minimum surface area per molecule of PGML was smaller than that of $C_{12}EO_n$ at the air/aqueous solution interface.

Novel 2-Pyrone Synthesis via the Nucleophilic Addition of Active Methine Compounds to 2-Alkynone, Iwao HACHIYA, Hitoshi SHIBUYA, and Makoto SHIMIZU, Tetrahedron Lett., 44, pp. 2061-2063, 2003.

Novel 2-pyrone synthesis via the nucleophilic addition of active methine compounds to 2-alkynone has been developed. The reaction of active methine compounds with 2-alkynone provided 2-pyrones in good yields. When malonic esters were used as a nucleophile, 5-alkoxycarbonyl-2-pyrones were obtained in good to high yields. On the other hand, the use of β-ketoesters as a nucleophile instead of malonic esters gave 5-acyl-2-pyrones in good yields. Even increasing the steric bulk of the nucleophile as with a 2-allyl-β-keto ester, the desired 2-pyrone was obtained in moderate yield. The reaction of Meldrum’s acid with 2-alkynone afforded the decarboxylated 2-pyrone in high yield.

Tandem N-Alkylation-C-allylation Reaction of α-Imino Esters with Organoaluminums and Allyltributyltin, Yasuki NIWA and Makoto SHIMIZU, J. Am. Chem. Soc., 125, pp. 3720-3721, 2003.

The tandem N-alkylation-C-allylation and N-alkylation-C-cyanation reactions of several α-imino esters with organoaluminums were carried out in good to excellent yields, where two nucleophiles attacked across the C=N double bond. The tandem reaction consists of the following three sequences: nucleophilic addition to the nitrogen atom of the imino ester, oxidation of the enolate with benzoyl peroxide, and allylation (or cyanation) to the resulting iminium salt. The aliphatic as well as aromatic imino esters underwent the tandem N-ethylation-C-allylation to give the addition products in moderate to good yields. To increase the utility of the tandem alkylation-allylation reaction, bis(trimethylsilyl)aluminum chloride was used as an initial N-alkylation reagent to afford the corresponding homoallylamines in good to high yields.

Design and Synthesis of 4,6-di-tert-Butyl-2,3-dihydro-5-benzofuranols as a Novel Series of Antiatherogenic Antioxidants, Kunio TAMURA, Yoshiaki KATO*, Akikra ISHIKAWA*, Yasuharu KATO*, Motomu HIMORI*, Mitsutaka YOSHIDA*, Yoshiaki TAKASHIMA*, Tsukasa SUZUKI*, Yoshiki KAWABE*, Osamu CYNSHI*, Tatsuhiko KODAMA*, Etsuo NIKI*, and Makoto SHIMIZU, J. Med. Chem., 46, pp. 3083-3093, 2003.

Antioxidants have been considered as potential antiatherogenic agents by inhibiting oxidation of low-density lipoprotein (LDL), albeit vitamin E, a natural antioxidant, has failed to show reduction on atherosclerosis in clinical trials. A novel series of antioxidants, 4,6-di-tert-butyl-2,3-dihydro-5-benzofuranols, were rationally designed and synthesized to overcome the clinical limitation of vitamin E. In vitro, the compounds showed a potent inhibitory effect on lipid peroxidation detected as 2-methyl-6-(p-methoxyphenyl)-3,7-dihydroimidazo[1,2-a]pyrazin-3-one (MCLA)-dependent chemiluminescence in linoleic acid autoxidation. In vivo, 4,6-di-tert-butyl-2,3-dihydro-2,2-dipentyl-5-benzofuranol (BO-653, 1f), an optimal compound, showed the highest concentration in plasma and LDL fraction in Watanabe heritable hyperlipidemic rabbits, due to its high affinity to LDL.

Double Nucleophilic Addition of Ketene Silyl (Thio)acetals and Trimethylsilyl Cyanide to α,β-Unsaturated Aldimines Promoted by Aluminum Chloride, Makoto SHIMIZU, Makiko KAMIYA, and Iwao HACHIYA, Chem. Lett., 32, pp. 606-607, 2003.

In the presence of $AlCl_3$, a mixture of ketene silyl (thio)acetal and trimethylsilyl cyanide underwent 1,4- and subsequent 1,2-additions, respectively, with α,β-unsaturated imines to give ethyl(*S*-alkyl) 5-amino-6-cyanopentanoates in good yields. Among the Lewis acids tested, $AlCl_3$ and TMSI were found to be efficient promoters. Although there was still much room for the improvement of diastereoselectivities, the use of imines having not only aromatic group but also aliphatic group worked well. In the case of the ketene silyl acetal derived from ethyl acetate, only 1,2-addition adduct was obtained. When ketene silyl thioacetals were used, the reaction proceeded to give 1,4-1,2-adducuts in moderate yields.

Facile Double Nucleophilic Addition of Thiols and Tetraallyltin to Latent 2-Alkynals Using in situ Hydrolysis of the Imino Functionality Promoted by Tin(IV) Chloride Pentahydrate, Makoto SHIMIZU, Takafumi NISHI, and Akihiro YAMAMOTO, Synlett, pp.1469-1473, 2003.

In the presence of $SnCl_4{\cdot}5H_2O$, a mixture of thiols and tetraallyltin underwent 1,4- and 1,2-additions, respectively, with the imines derived from 2-alkynals to give (*Z*)-1-sulfenyl-1,5-alkadien-3-ols in good yield, where the hydrolysis of the intermediary imino species was found to be crucial. Among the Lewis acids examined, $SnCl_4{\cdot}5H_2O$ gave the best result. The use of a mixed solvent system was also important to increase the product yield, and the reaction conducted in toluene-dichloromethane gave a better result. Under the optimum conditions found for the derivative of 3-phenylpropynal, the reactions gave the adducts with good to excellent (*Z*)-selectivities in good yields. The effects of acid additives are also noteworthy. The reaction conducted in the presence of pyridinium *p*-toluenesulfonate or 2,4,6-collidinium *p*-toluenesulfonate afforded the 1,4-1,2-addition products in higher yields, where the diastereoselectivities were somewhat lower.

Highly Chemoselective Crossed Pinacol Coupling Reaction Using the Synergetic Effect of Boron Trifluoride Etherate and Trichloromethylsilane, Makoto SHIMIZU, Ikuhiro SUZUKI, and Hiroaki MAKINO, Synlett, pp.1635-1638, 2003.

Use of boron trifluoride etherate and trichloromethylsilane in the presence of zinc-copper couple effected a crossed imino pinacol coupling reaction to give 1,2-diamines in good yields with high diastereoselectivities. The use of halogen as an electron-withdrawing substituent on the aromatic ring gave the unsymmetrical 1,2-diamines in good yield with high diastereselectivities. The use of the imine possessing a 2,4-dichlorophenyl moiety gave the crossed coupling product in low yield with low diastereoselectivity. The reaction of various imines with *N*-benzylidene-*p*-bromophenyl aniline usually proceeded to give the crossed coupling products in good yields. However, use of aliphatic and α,β-unsaturated aldimines did not give the desired coupling products.

Reductive Coupling of Acid Chlorides with nitriles Promoted by Titanium Tetra iodide. A Rapid Access to α-Imino Ketone, Makoto SHIMIZU, Nobuyuki MANABE, and Hiroshi GOTO, Chem. Lett., 32, pp. 1088-1089, 2003.

Reductive coupling reaction of carboxylic acid chlorides and alkyl nitriles were efficiently promoted by titanium tetraiodide to give α-imino ketones in good yields. When benzoyl chloride was treated with 2.0 equivalent of titanium tetraiodide in acetonitrile or propionitrile, the corresponding α-imino ketones were obtained in moderate yields, respectively. The reaction in isobutyronitrile gave the best yield of 61%. Pivalonitrile, a bulky nitrile, gave a lower yield. Reactions in nitriles possessing heteroatoms, such as chloroacetonitrile and methoxyacetonitrile, also proceeded to give the coupling products in moderate yields, whereas trichloronitrile did not give the desired product. When unsaturated nitriles such as acrylonitrile and crotononitrile were used, the coupling reaction did not proceed.

Photoinduced Intramolecular Electron Transfer between Carbazole and Bis(Trichloromethyl)-s-Triazine Generating Radicals, Koichi KAWAMURA, Yoshimasa AOTANI and Hideo TOMIOKA, J. Phys. Chem. B, 107, pp. 4579-4586, 2003.

An intramolecular electron transfer and photosensitivity in dye/initiator systems, in which an electron donating light-absorbing unit (carbazole) is tethered by methylene bonds to an electron-deficient initiator [bis(trichloromethyl)-*s*-triazine] was investigated. The efficient quenching of fluorescence was observed in the tethered compounds in a rigid matrix at low temperature, and the higher sensitivity of photopolymerization was observed in the photopolymer films containing the tethered compounds as photoinitiating systems compared with the films containing physical mixtures of dye and initiator. The compounds tethered by a longer methylene chain (C6 and C11) showed a higher photosensitivity than that tethered by a shorter methylene chain (C2 and C3), despite the efficient fluorescence quenching in the latter compounds. Control of back electron transfer after initial electron transfer or control of radiationless deactivation via exciplex formation was suggested to be important factor to design efficient dye-linked photoinitiators.

Triplet Carbenes: From Fleeting Existence to Attractive Molecular Units, Hideo TOMIOKA, Pure Appl. Chem., 75, pp. 1041-1047, 2003.

Attempts to stabilize the triplet state of carbenes to the extent that they can survive under normal conditions were made, in which triplet carbenes having a half-life of 19 min are realized. A way to use the resulting persistent carbene as a unit to construct photosensitive magnetic materials is also discussed.

Photochemical Transformations of Quintet *m*-Phenylenedinitrenes, Sergei V. CHAPYSHEV and Hideo TOMIOKA, Bull. Chem. Soc. Jpn., 76, pp. 2075-2089, 2003. (Best manuscript of the issue)

First photochemical transformations of quintet dinitrenes have been studied by FTIR spectroscopy during the photolysis of 1,3-diazidobenzene and its 2-methyl- and 2,4,6-trimethyl-substituted derivatives in solid argon at 12 K. The reactions involve two competitive processes. In the first one, the intramolecular insertion of the nitrene unit into 1,6-aromatic bond induces the ring-opening, which leads to the formation of iminoacetylenes. The second process involves the intramolecular addition of the nitrene unit to 1,2-aromatic bond followed by the ring-opening to form azirinobutadiene derivatives. Methyl groups in ortho-positions to the nitrene units of quintet dinitrenes efficiently protect their aromatic ring from nitrene attacks, substantially increasing the photochemical stability of such species. Thus, undesirable photochemical rearrangements of intermediate triplet azidonitrenes at early stages of the photolysis of 1,3-diazidobenzenes are completely suppressed on introducing the methyl group in position 2 of these azides.

Photolysis of Regioisomeric Diazides of 1,2-Diphenylacetylenes Studied by Matrix-Isolation Spectroscopy and DFT Calculations, Hideo TOMIOKA and Shinji SAWAI, Org. Biomol. Chem., 1, pp. 4441-4450, 2003.

A series of diazides of 1,2-diphenylacetylenes was photolyzed in matrices at low temperature, and transient photoproducts were characterized by using IR, UV/vis methods combined with ESR studies. Theoretical calculations were also used to understand the experimental findings. The introduction of phenylethynyl groups on phenyl azides shows little effect on the photochemical pathway. In marked contrast, azidophenylethylnyl groups exhibited a dramatic effect not only on the photochemical pathway of phenyl azides but also on the electronic and molecular structure of photoproducts. The patterns of the effect depended upon the relative position of azide groups in the diphenylacetylene unit.Whenever two azide groups were situated in a conjugating position with respect to each other, the azides always resulted in the formation of a quinoidal diimine diradical in which unpaired electrons were extensively delocalized in the π-conjugation.The *m,p'*-isomer was shown to be an excellent precursor for the high-spin quintet dinitrene. Moreover, the quintet bis(nitrene) was rather photostable under these conditions.

Triplet Carbene Surviving a Week in Solution at Room Temperature, Eri IWAMOTO, Katsuyuki HIRAI and Hideo TOMIOKA, J. Am. Chem. Soc., 125, pp. 14664-14665, 2003.

The stability of a triplet bis(anthryl)carbene was dramatically increased simply by introducing a group at its C_{10} position, where considerable spin density builds up and, hence, the carbene decays. 2,6-Dimethyl-4-tert-butylphenyl groups introduced at the C_{10} position of the triplet bis(anthryl)carbene are likely to quench almost any remaining decay pathways from this portion and make the triplet survive more than one week in solution at room temperature. This is the longest-lived triplet carbene. A light-induced generation of the stable triplet carbene opens a route to photosensitive organic magnetic materials.

Retardation Effect of Sulfonic Acid on Thermal Radical Polymerization of Styrene, Jun-ichi NAKAMIMA, Seiji TANIZAKI and Hideo TOMIOKA, J. Japan Petroleum Institute, 46, pp. 356-367, 2003.

A new polymerization retarder was investigated as an alternative to highly toxic dinitrophenols for the styrene distillation process. Dodecylbenzenesulfonic acid (DBS) was found to reduce the initial rate of thermal radical polymerization of styrene. The molecular weight of polystyrene resulting from thermal polymerization was slightly higher in the presence of DBS than in the absence of DBS. 1-Phenyltetraline (**1**), obviously produced by isomerization of the initial Diels-Alder adduct of styrene (**4**), was also detected in the presence of DBS. These observations suggest that DBS behaves as an acid catalyst for the isomerization of **4** to **1**. The retardation effect can be explained as the reduction of the concentration of initiate radicals generated from molecular assisted homolysis of **4** and monomeric styrene. Although only sulfonic acid cannot completely replace highly toxic and reactive dinitrophenols, it can reduce the amount of dinitrophenols required.

Computational Modeling of Phase Connectivity in Microstructures of Porous Materials during Sintering and Grain Growth, Masayoshi SHIMIZU, Hideaki MATSUBARA, Hiroshi NOMURA and Hideo TOMIOKA, J. Ceram.Soc. Jpn., 111, pp. 201-211. 2003.

A Mote Carlo simulation method using a three dimensional lattice was developed to analyze the connectivity of pores in sintered materials. The changes in porosity (f_V), mean grain diameter (D_S), intercept length of pores (D_V), contiguity of the solid phase (C) and fraction of connected pores ($f_{V,C}$) with the number of Monte Carlo steps (MCS) were analyzed as a function of initial porosity ($f_{V,0}$) and initial grain diameter ($D_{S,0}$). In many cases $f_{V,C}$ decreased with MCS down to 0 %, particularly at small and intermediate values of $f_{V,0}$ and $D_{S,0}$. However, in some cases of large $f_{V,0}$ and $D_{S,0}$, an $f_{V,C}$ of 100 % was maintained irrespective of MCS, which means that all pores may remain connected in the material. Systematic plots of D_V, D_S and C vs $f_{V,0} \times f_{V,C}$, which indicate the amount (%) of connected pores, are found to be useful for designing sintering and grain growth processes of porous materials.

Ab Initio Molecular Orbital Study on the G-Selectivity of GGG Triplet in Copper(I)-Mediated One-Electron Oxidation, Yasunori YOSHIOKA, Hiroko KAWAI, Tomoko SATO, Kizashi YAMAGUCHI*, and Isao SAITO*: J. Am. Chem. Soc., 125, pp.1968–1974, 2003.

The G-selectivity for Cu(I)-mediated one-electron oxidation of 5’-$TG_1G_2G_3$-3’ and 5’-$CG_1G_2G_3$-3’ has been examined by ab initio molecular orbital calculations. It was confirmed that G_1 is selectively damaged by Cu(I) ion for both 5’-$TG_1G_2G_3$-3’ and 5’-$CG_1G_2G_3$-3’, being good agreement with experimental results. The Cu(I)-mediated G_1-selectivity is primarily due to the stability of the Cu(I)-coordinated complex, $[-XG_1G_2G_3-,-Cu(I)(H_2O)_3]^+$. The Cu(I) ion coordinates selectively to N7 of G_2 of 5’-$G_1G_2G_3$-3’ rather than N7 of G_1. The G_2-selective coordination induces the G_1-selective trap of a hole that is created by one-electron oxidation and migrates to GGG triplet. Therefore, the radical cation of G_1 is selectively created in both 5’-$TG_1G_2G_3$-3’ and 5’-$CG_1G_2G_3$-3’, giving the G_1-selective damage of 5’-$G_1G_2G_3$-3’.

Thermal Reactions of 3-Furyl Fulgide and 3-Thienyl Fulgide. Ab Initio Molecular Orbital and CASSCF Studies, Yasunori YOSHIOKA, Mamoru USAMI*, Masayuki WATANABE*, and Kizashi YAMAGUCHI*: J. Mol. Struct. (THEOCHEM), 623, pp.167–178, 2003.

Thermal reactions of 3-furyl fulgide and 3-thienyl fulgide were examined at ab initio molecular orbital and CASSCF levels. The transition states of *EC* and *EZ*-isomerizations were determined by singlet UHF method with 6-31G* basis set, and their activation energies were successively estimated at CASSCF level. The geometries of the transition states of *EC*-isomerizations of 3-furyl fulgide and 3-thienyl fulgide are closer to those of *C*-isomers than those of *E*-isomers. The *EC*-isomerization proceeds in a conrotatory mode rather than a disrotatory mode due to steric repulsion of methyl groups, in conflict with the Woodward-Hoffmann selection rule. The activation energies of *EZ*-isomerizations are less by ~5 kcal/mol than those of *EC*-isomerizations, indicating that *EZ*-isomerizations are thermally preferred rather than *EC*-isomerizations, in harmony with thermal examinations of 3-furyl fulgide and 3-thienyl fulgide at 140 °C.

Theoretical Study of Role of H_2O Molecule on Initial Stage of Reduction of O_2 Molecule in Active Site of Cytochrome *c* Oxidase, Yasunori YOSHIOKA, Hiroko KAWAI, and Kizashi YAMAGUCHI*: Chem. Phys. Lett., 374, pp.45–52, 2003.

Mechanism of formation of [Fe-O-O-H, Cu_B] from [Fe-O-O, Cu_B] in active site of cytochrome *c* oxidase was theoretically investigated. It was found that the H_2O molecule is hydrogen-bonded to both Tyr244 and His290, and is a key molecule to produce Fe-O-O-H. This H_2O molecule plays a role as a carrier of a proton toward Fe-O-O to yield [Fe-O-O-H, Cu_B]. Cu_B atom is formally changed from cuprous state to cupric state through transportation of a proton by the H_2O molecule. A new reaction mechanism, which we call ‘water-proton transport’ (WPT) mechanism, is proposed for the initial stage of reduction of the O_2 molecule.

Theoretical Study of Hydrogen-Bonded Network and Proton Transfer in the Active Site of Reduced Cytochrome *c* Oxidase, Yasunori YOSHIOKA and Masaki MITANI: Internet Electron. J. Mol. Des., 2, pp.732–740, 2003.

There are many proposals of reaction mechanisms of O_2-reduction catalyzed by cytochrome *c* oxidase (C*c*O) and the mechanism is not still conclusive. We have previously proposed new ‘water-proton transport’ (WPT) mechanism in which H_2O hydrogen-bonded to His290 and Tyr244 transports a proton to FeOO to yield FeOOH. The path through which a proton is transferred to this H_2O molecule in the active site of C*c*O is investigated from theoretical viewpoint in this work by using the hybrid B3LYP method. The H_2O molecule exists between farnesylethyl and Thr316 by hydrogen bonds and the hydrogen-bonded network, which is connecting from Lys319 to the active site of O_2-reduction, is formed in the reduced C*c*O. The proton necessary for O_2-reduction is provided through this hydrogen-bonded network. The proton is trapped on farnesylethyl of heme a_3, subsequently the proton is transferred to Tyr244 to give a proton to the H_2O molecule between His290 and Tyr244. The energy barrier of the proton transfer is qualitatively estimated to be 12 kcal/mol.

Theoretical Molecular Auger Spectra with Electron Population Analysis, Masaki MITANI, Osamu TAKAHASHI*, Ko SAITO*, and Suehiro IWATA*: J. Electron Spectrosc. Relat. Phenom., 128, pp.103–117, 2003.

An approximation method is proposed to simulate the molecular Auger spectra. Auger transition rates are estimated with atomic populations of valence orbitals on an excited atom by Mulliken and Löwdin population analyses. Normal Auger energies and relative rates for H_2O and NH_3 molecules are evaluated using a full CI wave functions among the valence orbitals constructed from SCF orbitals for the neutral ground state and for the core-hole excited state. Theoretical spectra show fairly good correspondence with the experimental spectra. It is demonstrated that the present approach is applicable for qualitative assignment and analysis of Auger spectra for larger molecules.

Theoretical Studies on the Molecular Dependence of Bond Dissociation after Core Excitations II: $CH_3CO(CH_2)_nCN$, n = 0–3, Osamu TAKAHASHI*, Masanori JOYABU*, Masaki MITANI, Ko SAITO*, and Suehiro IWATA*: J. Comput. Chem., 24, pp.1329–1335, 2003.

Approximate theoretical normal and resonant Auger spectra for a series of methylcyano ketones were calculated. Compared with our previous procedure, a set of initial molecular orbitals (MOs) for Auger decay probability calculations of the normal Auger process was modified by changing from a set of ground state MOs to a set of core-holed MOs. For the resonant Auger process, a set of MOs was also modified in the same manner. Furthermore, the bond dissociation factor, which we introduced in the previous article, was also calculated to estimate the bond strength after Auger decay. The site-selectivity for a series of methylcyano ketones was qualitatively explained, but a significant state-specificity was not observed. Molecular size dependence after Auger decay was also discussed.

Theoretical Calculations of Effective Exchange Integrals by Spin Projected and Unprojected Broken-Symmetry Methods. I. Cluster Moldels of K_2NiF_4-Type Solids. Taku ONISHI, Daisuke YAMAKI*, Kizashi YAMAGUCHI*, and Yu TAKANO*: J. Chem. Phys., 118, pp. 9474-9761, 2003.

Previously, various symmetry-adapted (SA) and broken-symmetry (BS) computations have been performed for strongly correlated transition metal species so as to examine magnetic properties in simple cluster models. Though SA computations such as the complete active space configuration interaction (CAS CI) and CASSCF are desirable for estimating physical constants, these computations are heavy for larger cluster models with strongly correlated electrons. K_2NiF_4 is known to be the two-dimensional perovskite-type antiferromagnet and to have the electronic configuration similar to that of La_2CuO_4. Here, we have examined the utility and applicability of the BS spin-polarized hybrid-density functional theory (HUDFT) for cluster models of K_2NiF_4.

Theoretical Studies on the Electronic States of Electron-Doped Copper Oxides. Taku ONISHI, Daisuke Yamaki*, and Kizashi YAMAGUCHI*: Polyhedron., 22, pp. 2191-2197, 2003.

The infinite layer copper oxides have attracted much attention in relation to high-temperature superconductivity. Superconductivities of these species are achieved by several chemical dopings such as hole-doping and electron-doping. In this study, we have performed spin-polarized hybrid-density functional theory (HUDFT) calculations, in order to examine the electronic states after one electron-doping for the linear chain cluster models. As the hole-doped electronic states have already been examined in our previous work, we discuss the differences of the changes of the electronic states between hole-doping and electron-doping.

$Ln_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$(Ln=Pr, Nd, Gd; x=0.2, 0.3) for the Electrodes of Solid Oxide Fuel Cells, L. QIU, T. ICHIKAWA, A. HIRANO, N. IMANISHI, and Y. TAKEDA: Solid State Ionics, 158, pp. 55-65, 2003.

Promising candidates of intermediate temperature electrodes for solid oxide fuel cells (SOFCs), $Ln_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$(LSCF) (Ln=Pr, Nd, Gd; x=0.2, 0.3; $0 \leqq y \leqq 1$) were studied for their electrical conductivity, thermal expansion rate, cathodic polarization, and reactivity with gadolinia-doped ceria ($Ce_{0.9}Gd_{0.1}O_{1.95}$, CGO) or yttria-stabilized zirconia (YSZ). Superiorly electrical conductivity has been demonstrated for LSCF electrodes and all samples except Ln=Gd ($y \geqq 0.8$) compositions demonstrate above 200 S/cm at 800℃. The adjustment of thermal expansion rate to electrolyte, which is one of the main problems of $Ln_{1-x}Sr_xCoO_{3-\delta}$, can be achieved to lower thermal expansion coefficient (TEC) values with more Fe substitution. Using CGO electrolytes, LSCF electrodes over the composition range of y=0.0-0.8 show high cathodic activity for oxygen reduction operating at temperatures from 700 to 900℃ and exhibit no significant dependence on the kind of lanthanide elements. These electrode behaviors are analogous to widely used $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$, $Ln_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (Ln=Pr, Nd, Gd) systems, however, have potential advantages in reactivity with YSZ. In Ln=Pr, Nd (y=0.8) compositions, for example, the by-products of $Ln_2Zr_2O_7$ and $SrZrO_3$ are both suppressed when sintered at 1000℃ for 100 h. LSCF also yield no reaction product with CGO when sintered at 1200℃ for 36 h.

Compatibility of $Gd_xTi_2O_7$ Pyrochlores ($1.72 \le x \le 2.0$) as Electrolytes in High-Temperature Solid Oxide Fuel Cells, Masashi MORI*, Geoff M. TOMPSETT*, Nigel M. SAMMES*, Eisaku SUDA*, and Yasuo TAKEDA: Solid State Ionics, 158, pp. 79-90, 2003.

The crystal structure, sintering characteristics, electrical conductivity and thermal expansion of $Gd_xTi_2O_{7-\delta}$ pyrochlores ($1.72 \le x \le 2.10$) have been studied as potential electrolytes in high-temperature solid oxide fuel cells (SOFC). It was found that the A-site deficiency of $Gd_xTi_2O_{7-\delta}$ with cubic symmetry showed a wide region of $1.72<x<2.03$. A-site vacancies promoted the sintering characteristics of these materials. Electrical conductivity of the pyrochlores with A-site vacancies was lower than that of $Gd_xTi_2O_7$ in air although the reverse was observed in reducing atmospheres, due to the appearance of electronic conduction. Average linear thermal expansion coefficients of $Gd_xTi_2O_{7-\delta}$ pyrochlores decreased with increasing A-site vacancies. The difference between the TEC in air and in a H_2 atmosphere had a tendency to increase with increasing A-site vacancies.

Change in Conductivity of Yttria Stabilized Zirconia, Masatoshi HATTORI*, Yasuo TAKEDA, Satoshi OHARA*, Jin-Ho LEE*, Kazuo MUKAI*, Takehisa FUKUI*, Yoshinori SAKAKI* and Akihiro NAKANISHI*: Journal of the Japan Society of Powder and Powder Metallurgy, 50(4), p.297, 2003.

The change in conductivity of 8 mol% and 10 mol% yttria stabilized zirconia (8YSZ and 10YSZ, respectively) were measured during continuous current loading at 1000℃. The conductivity of 8YSZ gradually degraded with holding time in the test and it decreased to about 65% of the initial value after annealing for 1500 h. However, the conductivity of 10YSZ is constant under the same condition. The crystal structure of the samples before and after annealing was investigated by X-ray diffraction techniques, Transmission electron microscopy, and Raman spectroscopy. It was concluded that the deterioration in conductivity of 8YSZ related to the phase transformation, such as gradual formation of fine tetragonal phase which had lower conductivity than cubic phase had.

All Solid Lithium Polymer Batteries with a Novel Composite Polymer Electrolyte, Qi LI, Takahito ITO, Nobuyuki IMANISHI, Atsushi HIRANO, Yasuo TAKEDA, and Osamu YAMAMOTO*: Solid State Ionics, 159, pp. 97-109, 2003.

A composite polymer electrolyte based on polyethylene oxide (PEO) with a hyperbranched polymer poly[bis(triethylene glycol)benzoate] capped with an acetyl group (HBP) and a ceramic filler, $BaTiO_3$, was examined as the electrolyte in rechargeable lithium polymer batteries. The conductivity of the composite polymer electrolyte PEO-10 wt.% HBP with $Li(CF_3SO_2)_2N$-10 wt.% $LiPF_6$ as a lithium salt and 10 wt.% $BaTiO_3$ was found to be 1.6×10^{-4} S/cm at 25℃ and 1.5×10^{-3} S/cm at 60℃ in a O/Li ratio of 10. The lithium rechargeable batteries consisted of this highly conductive composite polymer electrolyte and the 4 V class cathode, $LiNi_{0.8}Co_{0.2}O_2$, showed excellent charge-discharge cycling performance. The initial cathode discharge capacity of 154 mA h/g declined only 0.1%/cycle during the first 30 cycles at 60℃.

DSC Study on the Thermal Stability of Solid Polymer Electrolyte Cells, C. CAPIGLIA, J. YANG, N. IMANISHI, A. HIRANO, Y. TAKEDA, and O. YAMAMOTO*: Journal of Power Sources, 119-121, pp. 826-832, 2003.

A novel Li-ion polymer battery (Li-IonPB) based on $LiNi_{0.8}Co_{0.2}O_2$ as a cathode and an alternative composite anode (CA) is proposed for future application in hybrid electric vehicles (HEV). A micro-Li-ion polymer cell is prepared in situ inside the differential scanning calorimetry (DSC) sample pan, and the exothermic heat development is compared with that of the micro-lithium-solid polymer electrolyte cell. The thermal decomposition of both cells is further investigated from a qualitative point of view.

High-Capacity Composite Anodes with SnSb and $Li_{2.6}Co_{0.4}N$ for Solid Polymer Electrolyte Cells, J. YANG, Y. TAKEDA, C. CAPIGLIA, X. D. LIU, N. IMANISHI, and O. YAMAMOTO*: Journal of Power Sources, 119-121, pp. 56-59, 2003.

Composite anodes based on SnSb alloy and $Li_{2.6}Co_{0.4}N$ compound can provide a reversible capacity more than 650 mAh/g in solid polymer electrolyte. However, the capacity retention on cycling is poor at a high-capacity level. Limited lithium insertion (<500 mAh/g) is favorable for the cyclability. Cyclic voltammetry of the composite electrode exhibits good electrochemical reversibility. Because the nano-sized $SiO_{1.1}$ host has a relatively small volume change effect and different insertion potential from SnSb and $Li_{2.6}Co_{0.4}N$, its addition in a small amount into the composite electrode can improve the mechanical and cycling stability.

Application of $La_{0.6}AE_{0.4}MnO_3$ (AE=Ca and Sr) to Electric Current Collectors in High-Temperature Solid Oxide Fuel Cells, Masashi MORI*, Nigel M. SAMMES*, Eisaku SUDA*, and Yasuo TAKEDA: Solid State Ionics, 164, pp. 1-15, 2003.

The crystallographic, mechanical, thermal and electrical properties of $La_{0.6}AE_{0.4}MnO_3$ perovskites (AE=Caa and Sr) have been investigated. $La_{0.6}Ca_{0.4}MnO_3$ showed an orthorhombic symmetry at room temperature, and its symmetry changed into tetragonal at approximately 500℃ and into cubic at approximately 900℃. $La_{0.6}Sr_{0.4}MnO_3$ showed tetragonal symmetry at room temperature and its symmetry changed into cubic at temperature ≥90℃. Transgranular fracture of dense $La_{0.6}AE_{0.4}MnO_3$ specimens, after mechanical strength measurements at temperatures ≤400℃, was indicated, whereas the specimens mechanically tested after the measurement at temperatures ≥600℃ showed intergranular fracture. Thermal expansion coefficients (TECs) of the sintered specimens in the temperature range from 50 to 1000℃ were 11.7×10^{-6}/℃ for $La_{0.6}Ca_{0.4}MnO_3$ and 12.2×10^{-6}/℃ for $La_{0.6}Sr_{0.4}MnO_3$. Electrical conductivities of the dense specimens at 1000℃ were 227 S/cm for $La_{0.6}Ca_{0.4}MnO_3$ and 213 S/cm for $La_{0.6}Sr_{0.4}MnO_3$. To synthesize these materials as electric current collectors in high-temperature solid oxide fuel cells(SOFC), $La_{0.6}AE_{0.4}MnO_3$ perovskites were compounded with manganese oxide. The TECs of the composites at around 50 vol.% Mn_3O_4 were almost the same as that of the Y_2O_3 stabilized ZrO_2 (YSZ) electrolyte. Electrical conductivities of these dense specimens at 1000℃ were observed to be between 50 and 90 S/cm. Thus, dense $La_{0.6}AE_{0.4}MnO_3$- Mn_3O_4 composites are appropriate for the electric current collectors in the SOFC.

Low-Temperature Sinterable $Ce_{0.9}Gd_{0.1}O_{1.95}$ Powder Synthesized through Newly-Devised Heat-Treatment in the Coprecipitation Process, Eisaku SUDA*, Bernard PACAUD*, Yvan MONTARDI*, Masashi MORI*, Masakuni OZAWA*, and Yasuo TAKEDA: Electrochemistry, 71(10), pp. 866-872, 2003.

The low-temperature sinterable $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO) Powder has been synthesized through a newly-devised heat-treatment process in the coprecipitation method. The precipitate obtained by the coprecipitation method, namely cerium-gadolinium carbonate slurry, was stirred at 80℃ for 3 h. After filtrating this slurry, the precipitate was washed using pure water and was calcined at 700℃ for 5 h in air. From the results of transmission electron microscopy and X-ray diffraction analysis, the CGO powder showed uniform particle size of approximately 100 nm and its crystallite size was calculated to be approximately 20 nm. For the tablet of the powder, the relative densities reached ≥ 94% at temperatures ≥ 1000℃ for holding time ≥ 5 h.

Laser Vaporization Synthesis of Polyhedral Graphite, Fumio KOKAI, Kunimitsu TAKAHASHI*, Daisuke KASUYA*, Atsuko NAKAYAMA*, Yoshinori KOGA*, Masako YUDASAKA* and Sumio IIJIMA*: Appl. Phys. A , 77, pp. 69-71, 2003.

Polyhedral graphite (PG) particles have been synthesized by CO_2 laser vaporization of graphite in high-pressure Ar gas (8×10^5 Pa). Faceted PG particles, ranging in size from 110 to 500 nm, have a turbostratic structure. The yield of PG is more than 90 %. This synthesis is based on the condensation of hot carbon species confined by an Ar-gas atmosphere.

Preparation of Lithium Niobate Thin Films on Diamond-Coated Silicon Substrate for Surface Acoustic Devices, Masatou ISHIHARA*, Takako NAKAMURA*, Fumio KOKAI and Yoshinori KOGA*: Diamond Related Materials, 12, pp. 1809-1813, 2003.

Lithium niobate ($LiNbO_3$) has a piezoelectric property, which makes it an ideal material for the fabrication of surface acoustic wave (SAW) devices. When highly oriented $LiNbO_3$ films are deposited on a diamond substrate, a $LiNbO_3$/diamond-layered structure is produced that can be used for wide-bandwidth applications in SAW devices at high frequencies. The $LiNbO_3$ thin films were deposited on diamond-coated silicon substrate by the radio-frequency reactive sputtering system. When a stoichiometric $LiNbO_3$ target was used as the sputtering target and the cooling efficiency of the target was poor, only $LiNbO_3$ reflections appeared in X-ray diffraction patterns. It is suggested that the appearance of the Li-deficient phase of $LiNbO_3$ is caused by the dissociation of lithium and oxygen from $LiNbO_3$ during deposition. When an Li-enriched $LiNbO_3$ target was used as the sputtering target and the cooling efficiency of the target was good, stoichiometric $LiNbO_3$ films were prepared and the preferential orientation was (110). It was found that the use of the Li-enriched target and the cooling of the target suppressed the dissociation of lithium.

Determination of Antimony in Waters by Electrothermal Atomic Absorption Spectrometry with Preconcentration on a Tantalum Wire, Md. Nurul AMIN, Satoshi KANECO, Ken NOMURA, Tohru SUZUKI and Kiyohisa OHTA: Mikrochim. Acta, 141, pp. 87–91, 2003.

A preconcentration method for antimony in waters involving adsorption on a tantalum wire, followed by electrothermal atomic absorption spectrometry with a tungsten tube atomizer is described. The best pH for the adsorption of antimony was 2. The optimal immersing time was 120 s. Under the optimal conditions, the detection limit for antimony by the tantalum wire preconcentration method was 50 pg/mL (3S/N) and the relative standard deviation was 9.4%. The effects of large amounts of concomitants on the preconcentration of antimony were evaluated. Even though 103-104 fold excess of matrix elements existed in water, the antimony response was not significantly affected by the matrix elements. The method with preconcentration on a tantalum wire was applied to the determination of antimony in waters and proved to be sensitive, simple, and convenient. This adsorption method can be utilized in in-situ sampling of ultra-trace antimony in environmental samples (water). Furthermore, after sampling it is easy to carry and store the tantalum wire without contamination for a long time. The technique developed was shown to be useful for the determination of Sb in waste waters at the 1-5 μg/L level.

High-Efficiency Electrochemical CO_2-to-Methane Reduction Method Using Aqueous $KHCO_3$ Media at Less Than 273 K, Satoshi KANECO, Nobuhide HIEI, Yue XING, Hideyuki KATSUMATA, Hisanori OHNISHI, Tohru SUZUKI and Kiyohisa OHTA: J. Solid State Electrochem., 7, pp. 152–156, 2003.

The electrochemical reduction of CO_2 with a Cu electrode in a $KHCO_3$ aqueous solution was investigated at low temperature. A divided H-type cell was employed; the electrolyte was a 1.1 mol dm^{-3} $KHCO_3$ aqueous solution. The temperature during the electrolysis of CO_2 was reduced to 269 K. Methane, ethylene, and formic acid were obtained from CO_2 as the main products. The maximum faradaic efficiency of methane was 44% at a relatively negative potential and 269 K. The efficiency of hydrogen formation, as the competition against CO_2 reduction, significantly decreased with lowering the temperature. On the basis of this work, the high-efficiency electrochemical CO_2 to methane conversion method appears to be achieved.

Removal of Natural Organic Polyelectrolytes by Adsorption onto Tobermorite, Satoshi KANECO, Kumiko ITOH, Hideyuki KATSUMATA, Tohru SUZUKI, Kazuaki MASUYAMA*, Kunihiro FUNASAKA*, Kazuyuki HATANO* and Kiyohisa OHTA: Environ. Sci. Technol. (American Chemical Society), 37, pp. 1448–1451, 2003.

Natural organic polyelectrolytes, such as humic and fulvic acids, were removed by adsorption onto silicate rocks. Tobermorite, zeolite, and molecular sieves 5A were used as the adsorbents. Tobermorite was more efficient by 40‒50% in the removal of fulvic acids, and by 30~50% for humic acid than zeolite or molecular sieves, respectively. Humic acid removal from the solution by adsorption onto silicate rocks took place more readily than fulvic acid removal. From the determined heat of adsorption, the adsorption process in the present study may be chemisorption (ligand exchange). Metal/humic acid complexes was effectively removed by adsorption onto tobermorite. Since tobermorite (a silicate rock) can be easily synthesized and obtained commercially, the adsorption method of fulvic and humic acids is superior to their precipitation.

Sunlight Photocatalytic Degradation of Bisphenol A in Water with Titanium Dioxide, Satoshi KANECO, Yasumasa FUJIWARA, Tohru SUZUKI, Hideyuki KATSUMATA, Kunihiro FUNASAKA* and Kiyohisa OHTA: ITE Lett. Batt. New Technol. Med., 4, pp. 211–214, 2003.

The photocatalytic degradation of 4,4’-isopropylidenediphenol (bisphenol A) in aqueous solutions with TiO2 semiconductors was investigated under sunlight illumination. It was found that the primary photocatalytic decomposition reaction follows a pseudo first-order kinetic law. During the photocatalytic degradation, the first-order rate constant k was 0.025 min^{-1}. The present detoxification method will be able to be applied to various endocrine-disrupting chemicals.

Carbon Dioxide Sequestration Technology by Electrochemical Conversion at Cadmium Electrode in Methanol under Mild Conditions, Satoshi KANECO, Ryosuke IWAO, Hideyuki KATSUMATA, Tohru SUZUKI and Kiyohisa OHTA: Photo/Electrochem. Photobiol. Environ. Energy Fuel, 2, pp. 181－189, 2003.

The electrochemical reduction of CO_2 in a KOH/methanol-based electrolyte was investigated with a cadmium wire electrode at ambient temperature and pressure. Carbon monoxide, formic acid and methane were the main products from the CO_2. The Faradaic efficiency of formic acid increased as the potential became negative, however in contrast the formation efficiency of CO deceased. Under the optimum experimental conditions, 64 % Faradaic efficiency formic acid, 48 % CO and 0.2 % methane were produced from CO_2 by the electrochemical reduction. Hydrogen evolution in competition with CO2 reduction was observed at only a 0.9 % Faradaic efficiency. The partial current density for the CO_2 reduction was more than 109 times greater than that for hydrogen evolution. Future work to advance this technology may include the use of solar energy as the electric energy source. This research can contribute to applications of the conversion of CO_2-saturated methanol into useful products and the large-scale removal of CO_2 from the atmosphere.

Continuous Degradation of Chlorodibromomethane in a Flow System Using Zinc Powder under Mild Conditions, Ahmed H.A. DABWAN, Tohru SUZUKI, Satoshi KANECO, Hideyuki KATSUMATA and Kiyohisa OHTA: Photo/Electrochem. Photobiol. Environ. Energy Fuel, 2, pp. 163－171, 2003.

The continuous destruction of chlorodibromomethane in a flow system using zinc metallic powder was investigated under mild conditions. The dechlorination efficiency increased with increasing temperature up to 35 ^{o}C. Consequently, it was found that chlorodibromomethane could be almost completely degraded in the continuous flow system using the zinc powder above 35 ^{o}C. The continuous complete decomposition treatment of chlorodibromomethane could be performed for 12 h. This research will be able to contribute to the treatment technology of chlorodibromomethane-contaminated ground water.

Slurry Sampling Electrothermal Atomic Absorption Spectrometric Determination of Copper in Herbal Medicine Samples with a Molybdenum Tube Atomizer, Md. Nurul AMIN, Satoshi KANECO, Tohru SUZUKI and Kiyohisa OHTA: Microchim. J., 74, pp. 181-186, 2003.

An ultrasonic slurry sampling electrothermal atomic absorption spectrometric method with a molybdenum tube atomizer has been developed for the determination of copper in herbal medicine samples. Glycerol solution (10%) was used as the slurry medium. The optimum pyrolysis temperature was 760 °C. The detection limit was 72 fg (3×S/N ratio). Matrix element interference was investigated and it was found that glycerol as a chemical modifier eliminated the interference. The amounts of copper in herbal medicines determined by the method proposed are in good accordance with those measured in dissolved acid-digested samples. The method enables rapid calibration, and simple and rapid analysis of copper in herbal medicine samples at low cost.

Degradation of $CHBrCl_2$ in a Continuous Flow System Using Metal Powder under Mild Condition, Ahmed H.A. DABWAN, Tohru SUZUKI, Satoshi KANECO, Hideyuki KATSUMATA and Kiyohisa OHTA: ITE Lett. Batt. New Technol. Med, 4, pp. 461–464, 2003.

The continuous destruction of bromodichloromethane in a flow system using nickel, zinc and Ag/Zn bimetal powders was investigated under mild conditions. Bimetallic Ag/Zn was very effective for the continuous degradation of bromodichloromethane. The yields for bromide and chloride ions were greater than 70 and 96% in the continuous degradation using bimetallic Ag/Zn, respectively. The continuous decomposition treatment of bromodichloromethane could be performed with a relatively high efficiency for 12 h. This research will be able to contribute to the treatment technology of bromodichloromethane-contaminated ground water.

Size Distributions and Characteristics of Atmospheric Inorganic Particles by Regional Comparative Study in Urban Osaka, Japan, Kunihiro FUNASAKA*, Mamoru SAKAI*, Masanao SHINYA*, Takeji MIYAZAKI*, Toshikazu KAMIURA*, Satoshi KANECO, Kiyohisa OHTA and Tadao FUJITA: Atmos. Environ., 37, pp. 4597–4605, 2003.

Size distributions and characteristics of atmospheric inorganic particles at two different monitoring sites were statistically compared in order to survey site-specific original sources of the particulate constituents. The average concentration difference of fine and coarse particles between the sites was, respectively, 1.4 and 4.7 $\mu g/m^3$, and coarse particulate Fe, Mn, Zn and Pb were significantly high at the heavy traffic-flow site. Coarse particulate Zn and Pb form a closely related cluster group but Mn belongs to another independent group together with Fe. Comparative study for the Zn/Pb ratio possibly suggested that the regional differences of Zn and Pb were derived from road dust components and this might be caused essentially by tire wears and previous lead additives, respectively. On the contrary, the differences of coarse particulate Fe and Mn might be commonly and directly affected by industrial sources such as iron–steel factories close to the heavy traffic-flow site.

Electrothermal Atomic Absorption Spectrometric Determination of Cadmium in Bangladeshi Vegetables with a Metal Tube Atomizer And Slurry Sampling Technique, Md. Nurul AMIN, Satoshi KANECO, Tohru SUZUKI and Kiyohisa OHTA: Int. J. Environ. Anal. Chem., 83, pp. 1035－1044, 2003.

Ultrasonic slurry sampling electrothermal atomic absorption spectrometry with a molybdenum tube atomizer has been applied for the determination of cadmium in vegetable samples in Bangladesh. The suspension-stabilizing medium was 10% glycerol solution. The optimum pyrolysis temperature was 300 °C. The detection limit was 13 fg (3S/N). Matrix element interference was studied and it was found that thiourea as a chemical modifier eliminated the interference. The results for the determination of cadmium in vegetable samples by the proposed method were in good agreement with those measured in dissolved acid-digested samples. The method enables rapid calibration, and simple and rapid analysis of cadmium in vegetable samples at low cost.

Biodegradation of Phthalic Acid Esters by Bakery Yeast *Saccharomyces cerevisiae*, Aleya BEGUM, Hideyuki KATSUMATA, Satoshi KANECO, Tohru SUZUKI and Kiyohisa OHTA: Bull. Environ. Contam. Toxicol., 70, pp. 255–261, 2003.

Biodegradation of phthalic acid esters (PAEs), namely diethyl phthalate (DEP), di-n-butyl phthalate (DBP) and butylbenzyl phthalate (BBP) was performed by *Saccharomyces cerevisiae*. The degradation reaction of PAEs followed a first order kinetic law and the degradation rate was DBP>BBP>DEP. The half-lives of DEP, DBP and BBP were 56, 16, 22 h, respectively.

Removal of Organic Polyelectrolytes and Their Metal Complexes by Adsorption onto Xonotlite, Hideyuki KATSUMATA, Satoshi KANECO, Rika MATSUNO, Kumiko ITOH, Kazuaki MASUYAMA*, Tohru SUZUKI, Kunihiro FUNASAKA* and Kiyohisa OHTA: Chemosphere, 52, pp. 909–915, 2003.

Natural organic polyelectrolytes (humic and fulvic acids) and their metal complexes were removed by adsorption onto xonotlite. The removal percentages of humic and fulvic acids by xonotlite were ca. 80 and 30%, respectively. Humic acid removal from solution by adsorption onto xonotlite took place more readily than fulvic acid removal. The molecular weight distributions of the humic substances remaining in solution after adsorption with the xonotlite were measured with size exclusion chromatography. A comparison of molecular weight distributions demonstrated conclusively that large molecular weight components were adsorbed preferentially, indicating that adsorption efficiency depends on the number of functional groups of humic substances. Furthermore, the surface topography of the adsorbent was observed before and after adsorption by scanning electron microscopy. The calculated heat of adsorption was of 330 kJ mol^{-1} which was evaluated from the Clapeyron-Clausius equation. Therefore, the adsorption type can be considered chemical. Since xonotlite can be easily synthesized and obtained at low cost, the adsorption method of humic and fulvic acids is superior to their precipitation.

Formation of Dioxins from Newspaper Combustion in the Presence of Sodium Chloride and Poly (Vinylidene Chloride), Hideyuki KATSUMATA, Makoto YABUUCHI, Satoshi KANECO, Tohru SUZUKI and Kiyohisa OHTA: Fresenius Environ. Bull., 12, pp. 406–412, 2003.

Exhaust gases from the combustion of newspapers alone, from newspapers impregnated sodium chloride (NaCl), and from newspapers mixed with poly (vinylidene chloride) (PVDC) were collected. The samples were analyzed for dioxins by high-resolution gas chromatography/mass spectrometry. Total amounts of dioxins found in the samples were 21.6 pg g^{-1} from newspapers alone, 51.9 pg g^{-1} from newspapers with NaCl, and 1525 pg g^{-1} from newspapers with PVDC. It is postulated that there is a correlation between dioxin formation and chloride content. Formation of total PCDFs was considerably higher than that of total PCDDs, except in the case of newspapers alone. The total PCDF/total PCDD ranged from 0.16 (newspaper alone) to 16.4 (newspaper with PVDC). These results indicate that NaCl and PVDC contribute significantly to dioxin formation from waste materials combusted in incinerators.

Air Pollution by Dioxins at Various Locations Using Polyurethane Foam as A Monitoring Indicator, Hideyuki KATSUMATA, Hidetoshi OKADA, Satoshi KANECO, Tohru SUZUKI and Kiyohisa OHTA: Photo/Electrochem. Photobiol. Environ. Energy Fuel, 2, pp. 173－180, 2003.

Evaluation method of air pollution by dioxins was proposed by using polyurethane foam as a monitoring indicator. This sampling method is based on the adsorption of dioxins in atmosphere to the polyurethane. Collection of dioxins by the polyurethane foam was performed at three sites in Hisai City, Mie Prefecture, where are near the incinerator, for two to four weeks. In the sampling period of two weeks, adsorption amounts of dioxins on the polyurethane at Site 1, 2 and 3 were 4.47, 25.9 and 3.52 pg cm^{-2}, respectively. 4CDD/F isomers predominantly adsorbed at all sites and it was observed that the adsorption amount of PCDD/Fs was decreased with increasing the number of chloride. Furthermore, the distribution pattern of 4CDD isomers at Site 2 was investigated. The 1,3,6,8- and 1,3,7,9-isomers composed over 75% of the total isomers of 4CDD. This pattern might show that the 4CDD was mainly derived from chloronitrophene, which is a kind of pesticides.

Removal of Heavy Metals in Rinsing Wastewater from Plating Factory by Adsorption with Economical Viable Materials, Hideyuki KATSUMATA, Satoshi KANECO, Kentaro INOMATA, Kumiko ITOH, Kunihiro FUNASAKA*, Kazuaki MASUYAMA*, Tohru SUZUKI and Kiyohisa OHTA: J. Environ. Manage., 69, pp. 187–191, 2003.

The removal of heavy metals from plating factory wastewater with economical materials was investigated by the column method. Montmorillonite, kaolin, tobermorite, magnetite, silica gel and alumina were used as the economical adsorbents to wastewater containing Cd(II), Cr(VI), Cu(II) and Pb(II). This removal method of heavy metals proved highly effective as removal efficiency tended to increase with increasing pH and decrease with increasing metal concentration. The removal percentages by adsorption onto montmorillonite, tobermorite, magnetite, and silica gel showed high values for all metals. From the results for the heat of adsorption, the adsorption process in the present study might be chemisorption. The proposed method was successfully applied to the removal of Cd(II), Cr(VI) and Cu(II) in rinsing wastewater from plating factory in Nagoya City, Aichi Prefecture, Japan. Since the economical adsorbents used can be obtained commercially because they are easily synthesized, the wastewater treatment system developed is rapid, simple and cheap for the removal of heavy metals.

Removal of Di-*n*-butyl Phthalate from Aqueous Solution by Adsorption with Bakers' Yeast *Saccharomyces cerevisiae*, Aleya BEGUM, Hideyuki KATSUMATA, Nozomu SAKUMA, Satoshi KANECO, Tohru SUZUKI and Kiyohisa OHTA: Photo/Electrochem. Photobiol. Environ. Energy Fuel, 2, pp. 155－162, 2003.

The adsorption behavior of two phthalic acid esters (PAEs) namely, diethyl phthalate (DEP) and di-*n*-butyl phthalate (DBP) from aqueous solution to baker's yeast (*Saccharomyces cerevisiae*) was quantitatively characterized in this work. The effects of yeast amounts, pH values, culture time, temperature and initial PAEs concentrations were studied. The experimental results showed that the adsorption efficiency of DBP was much higher than that of DEP. Therefore, the present method could be selectively adsorb the DBP to *S. cerevisiae*. Clausius-Clapeyron equation was applied to estimate the heat of adsorption. The heat of adsorption of DBP was 373 kJ mol^{-1}, indicating that the adsorption behavior seemed to be chemical adsorption.

Microbial Metabolism of Phthalic Acid Esters by Bakers' Yeast *Saccharomyces cerevisiae*, Aleya BEGUM, Hideyuki KATSUMATA, Satoshi KANECO, Tohru SUZUKI and Kiyohisa OHTA: Fresenius Environ. Bull., 12, pp. 1309–1314, 2003.

Microbial metabolism behavior of two phthalic acid esters (PAEs) namely, diethyl phthalate (DEP) and butylbenzyl phthalate (BBP) from aqueous solution by bakers' yeast *Saccharomyces cerevisiae* was quantitatively characterized by high performance liquid chromatography (HPLC). The optimal culture temperature, amount of yeast, yeast growth time, and ammonium dihydrogen phosphate (ADP) amount, that can influence on biodegradation of PAEs were 30 ^{0}C, 2.0 mg mL^{-1}, 30 min, and 0.5 mg mL^{-1}, respectively. Under the optimal conditions, the degradation percentage of DEP and BBP were 19% and 43%, respectively after 24 h cultivation. The metabolites of DEP degradation as identified by gas chromatography-mass spectrometry (GC/MS) appeared to be ethyl methyl phthalate (EMP), dimethyl phthalate (DMP) and phthalic acid (PA), whereas monobutyl phthalate (MBP), diethyl phthalate (DEP) and phthalic acid (PA) were identified as metabolites of BBP. Therefore, it can be considered that one of the degradation pathways involves sequential cleavage of the ester bond to yield PA.

Two-Dimensional High Performance Liquid Chromatography Mapping of Sugar Chains Demonstrated the Biantennary, Complex N-Glycan Addition to the Recombinant Glycoprotein Produced by Baculovirus-Infected *Antheraea pernyi* Insect Cells, Masahiro NAGAYA, Jun KOBAYASHI, Noriko TAKAHASHI*, Koichi KATO* and Tetsuro YOSHIMURA: Journal of Insect Biotechnol. & Sericol., 72, pp. 79-86, 2003.

To evaluate the N-glycosylation property of an insect cell line, AnPe, which was derived from embryos of the Chinese oak silkworm *Antheraea pernyi* and used in a newly developed baculovirus expression vector system, N-glycans of purified PTTH produced by AnPe cells infected with a recombinant AnpeNPV, were digested with glycoaminase A, reductively aminated with 2-aminopyridine, and identified by 2D-HPLC mapping technique, and the result that a reaction catalyzed by GlcNAc transferase II, a key enzyme to form biantennary, complex N-glycans, occurs more efficiently in AnPe than in Sf9 was obtained, suggesting that the proportion of complex N-glycans in AnPe cells may be largely enhanced by inhibiting the N-acetylglucosaminidase activity and/or supplying sufficient amounts of enzymes and substrates required for the sugar chain extension in the Golgi.

Antheraea pernyi Nucleopolyhedrovirus p143 Gene: Nucleotide Sequence and Ineffectiveness in Host Range Expansion of *Autographa californica* Nucleopolyhedrovirus. Ken-ichi MAEGAWA, Jun KOBAYASHI and Tetsuro YOSHIMURA: Int. J. Wild Silkmoth & Silk, 8, pp. 29-41, 2003

The nucleotide sequences of 3.2- and 4.9-kbp PstI P and H fragments of the AnpeNPV containing the p143 gene were determined. A putative DNA helicase of 1212 amino acids was encoded by the gene and exhibited high sequence identities of 58% to 78% with the p143 gene products of other group I NPVs. Seven conserved helicase motifs, a leucine zipper motif, and two nuclear localization signals, which are conserved among the baculovirus DNA helicases, were also found in the AnpeNPV p143 gene product. The AnpeNPV p143 gene introduced in the AcNPV genome were co-expressed with the AcNPV p143 at early phase of infection, but did not enhance either BV production at late phase or recombinant protein production at very late phase in AnPe cells. Thus, the AnpeNPV p143 gene was not effective in host range expansion of AcNPV to semipermissive AnPe cells, although the results was not conclusive.

Efficient Production of Monoclonal Antibodies Specific to Aimed Epitope Sequences by a B Cell Targeting Technique. Masahiro TOMITA, Takanobu TANIGUCHI, Jun-ichiro TANAKA, Hana SAWADA*, Norikazu NISHINO* and Tetsuro YOSHIMURA: Peptide Science 2002, pp.397-400, 2003.

Human insulin consists of 51 amino acid residues, and has been shown to harbor several differences in amino acid residues from mouse insulin. When the mouse immune system recognizes human insulin as a foreign antigen, such regions must play an important role in humoral immunity for producing antibodies specific to human insulin. A BLAST (Basic Local Alignment Search Tool) analysis is one of the simplest and the most available methods for predicting epitope sequences in an antigen of interest. We focused on generating monoclonal antibodies specific to desired epitope sequences of human insulin by a B cell targeting technique. The hybridoma cells secreting monoclonal antibodies against the aimed peptide sequences were successfully obtained, although the specificity was rather polyreactive.

Generation of Monoclonal Antibodies Directed against Peptide Sequences by a B Cell Targeting Technique. Masahiro TOMITA, Takanobu TANIGUCHI, Jun-ichiro TANAKA, Hana SAWADA*, Norikazu NISHINO*, Tian Yow TSONG* and Tetsuro YOSHIMURA: Human Antibodies, 12, pp.37-39, 2003.

Two putative eiptope sequences in human insulin that are VNQHLCG and FFYTPKT were constructed based on a BLAST (Basic Local Alignment Search Tool) analysis. Firstly, the targeting of B lymphocytes by these epitope sequences after in vitro immunization was immunofluorescently confirmed, and then the peptide-selected B lymphocytes were combined with myeloma cells by exploiting the specificity and strength of the interaction between biotin and avidin. These cell complexes were selectively fused by an electrical pulse. Several clones secreting monoclonal antibodies against each peptide sequence were successfully obtained, although they showed rather polyreactive specificities. We suggest that the targeting technique have driven efficient production of monoclonal antibodies against the peptide sequences even after short immunization.

NTP Concentration Switches Transcriptional Activity by Changing the Large-Scale Structure of DNA, Tatsuo AKITAYA*, Kanta TSUMOTO, Ayako YAMADA*, Naoko MAKITA*, Koji KUBO* and Kenichi YOSHIKAWA*: Biomacromolecules, 4, pp. 1121-1125, 2003.

It is becoming clearer that genetic activity is closely associated with the intracellular energy state. However, the mechanisms of this association are still unclear. In this study, we focused on large-scale changes in the structure of DNA to examine the effect of the NTP concentration on the transcription reaction with T7 RNA polymerase and compared the results with long duplex DNA to those with a short persistent-length fragment. The transcriptional activity dramatically changed only for long duplex DNA within a narrow range of NTP concentrations associated with changes in the large-scale structure of DNA. This result suggests that the energy state may play an essential role in regulating ON/OFF switching on transcriptional activity.

Giant DNA Molecules Exhibit On/Off Switching of Transcriptional Activity through Conformational Transition, Kanta TSUMOTO, François LUCKEL* and Kenichi YOSHIKAWA*: Biophys. Chem., 106, pp. 23-29, 2003.

We found that the transcriptional activity of large DNAs (40 kbp) can be completely inhibited by adding condensing agents, spermine and poly(ethylene glycol), whereas under the same conditions short fragments (140 bp) still show active transcription. Fluorescence microscopic observations of large DNAs revealed clear correlation between the higher-order structure of templates and their transcriptional activity. The steep decrease in transcriptional activity leading to complete inhibition, or on/off switching, is interpreted in terms of conformational transition of the ensemble of DNA molecules.

Gene Expression within Cell-Sized Lipid Vesicles, Shin-ichiro M. NOMURA*, Kanta TSUMOTO, Tsutomu HAMADA*, Kazunari AKIYOSHI*, Yoichi NAKATANI* and Kenichi YOSHIKAWA*: ChemBioChem, 4, pp. 1172-1175, 2003.

Functional protein synthesis was observed in cell-sized lipid vesicles following encapsulation of a gene-expression system. Expression of rsGFP (red-shifted green fluorescent protein) within individual vesicles was observed by fluorescence microscopy. Interestingly, at the early stage of the reaction, the expression efficiency inside the vesicle was remarkably higher than that in the solution outside. The synthesized rsGFP in individual vesicles is safe from attack by proteinase K added to the external aqueous solution. Studies on cell-sized vesicles expressing protein should contribute to a fundamental understanding of certain aspects of living systems and will be useful for practical applications, such as the construction of microreactors.

Surfactant Properties of Purified Polyglycerol Monolaurates, Tomoharu KATO, Takeshi NAKAMURA*, Masatsugu YAMASHITA*, Masami KAWAGUCHI, Tadaya KATO, and Takahito ITOH: J. Surfactants Detergents, 6, pp 331 – 337, 2003.

A series of purified polyglycerol monolaurates (PGML), such as di-, tri-, tetra, and pentaglycerol monolaurates, were synthesized, and their surfactant properties in aqueous solutions were examined. The surfactant properties of PGML were compared with those of n-dodecyl polyoxyethylene monoethers ($C_{12}EO_n$) to examine the function of the hydrophilic part of these compounds. The critical micelle concentration (CMC) values and the surface tension at CMC of PGML and $C_{12}EO_n$ increased linearly with an increase in the number of glycerol and oxyethylene units, respectively. The initial foam heights of the surfactants at the CMC increased with an increase in the number of glycerol and oxyethylene units. and the foam heights of PGML were consistently higher and more stable than those of $C_{12}EO_n$. Triglycerol monolaurate showed the lowest interfacial tension and the highest detergency among all of the surfactants tested. Therefore, the PGML showed better performance in all the surfactant properties tested than $C_{12}EO_n$.

Structural Regulation of Peptide-Conjugated Graft Copolymer: A Simple Model for Amyloid Formation, Tomoyuki KOGA*, Kazuhiro. TAGUCHI*, Yoshiaki KOBUKE*, Takatoshi KINOSHITA*, and Masahiro HIGUCHI, Chem. Eur. J., 9, pp. 1145-1156, 2003.

We successfully synthesized a novel artificial protein model, polyglutamate-grafted polyallylamine **(1)**, and described its structural and conformational properties in solutions. The secondary and quaternary structures of the peptide **1** can be easily controlled by manipulating the pH, solution composition, and salt concentration. Only under the condition of low pH (< 8) or that of low salt concentration (< 30 mM) did the electrostatic repulsive force based on the protonated amino groups permit the controlled growth of **1**-aggregates and the tight packing of hydrophobic PMLG chains, resulting in induction of highly-ordered fibril formation with α-to-β structural transition. These findings strongly suggest that the formation of fibril structure is not restricted to specific protein sequences but is, rather, a common property of polypeptides. The ability to control the distribution of high-order structures of the model peptide formed by manipulating environmental conditions or intermolecular interaction should provides important insights not only for understanding the assembly mechanism of peptides and proteins, but also for developing novel peptide-based material with well-defined nanostructures.

The Formation of Gold Metal Fibers During the Production of E-Glass Fibers, Hiroshi ASAO and Kanichi KAMIYA: Adv. Composite Mater., 12, pp.1-12, 2003.

We first examined the relation between the solubility of gold and the reduction-oxidation (redox) condition of E-glass, but it was difficult to find a universal relation between the gold solubility and the redox of the glasses. Next, we examined the relation between the solubility of gold and the theoretical optical basicity of the glass and found that the theoretical optical basicity of the glasses was closely related to the gold solubility. We discussed the mechanism of increasing the solubility of the gold, probably through the formation of some complex with oxide ions. In the industrial process, no metal fiber was formed when glass composition of theoretical optical basicity larger than about 0.60l was spun.

Surface Properties of Polydimethylsilloxane-Based Inorganic/Organic Hybrid Films Deposited on Polyimide Sheets by the Sol-Gel Method, Takuya SHINDOU, Shingo KATAYAMA*, Noriko YAMADA* and Kanichi KAMIYA: J. Sol-Gel Science and Technology, 27, pp. 15-21, 2003.

Polydimethylsiloxane (PDMS)-based inorganic/organic hybrids films were prepared on polyimide sheets by the sol-gel method using silanol-terminated PDMS and titanium tetraisopropoxide as starting materials. The effect of heat-treatment temperature on the surface property of the hybrid films was examined in terms of contact angle of water and Tapping-Mode Atomic Force Microscopy (AFM). AFM phase images showed the presence of domains, 200-500 nm in size, on the surface of these films after heat-treatment below 300°C. These regions were more hydrophilic than the rest of the area. The domains disappeared at 300°C and the surface became homogeneous surface of the peak to valley value about 10 nm. The films were hydrophobic, and a maximum contact angle (about 115°C) was obtained.

Photoinduced Phenomena in Na_2S-GeS_2 Glasses, Keiji TANAKA*, Noriyuki NEMOTO* and Hiroyuki NASU: Jpn. J. Appl. Phys., 42, pp. 6748-6752, 2003.

Composition dependence of physical properties and photoinduced phenomena in ionic chalcogenide glasses, Na_2S-GeS_2, has been studied. The density, optical gap, and photoinduced phenomena show characteristic changes at around $10Na_2S$-$90GeS_2$. In the glasses with greater Na_2S contents, photoenhanced hydration occurs. Photoinduced birefringence is maximal at $20Na_2S$-$80GeS_2$. Origins of these features are discussed on the bases of atomic and electronic models.

Non-Linear Optical Properties of Li_2O-TiO_2-P_2O_5 Glasses, Nobuhiro SHIMOJI, Tadanori HASHIMOTO, Hiroyuki NASU and Kanichi KAMIYA: J. Non-Cryst. Solids, 324, pp. 50-57, 2003.

The non-linear optical properties of Li_2O-TiO_2-P_2O_5 glasses were measured by Z-scan technique using a nano-second pulsed laser. The non-linear refractive index (γ_Z) estimated from Z-scan normalized transmittance was considered to include the optical Kerr effect (γ_K), the thermo-optic effect (γ_T) and the resonant non-linearity (γ_R) related to Ti^{3+} ions of which content was increased with TiO_2 content. The sign of γ_Z for glasses with 5 and 10mol% TiO_2 was positive, whereas for glasses with 15 and 20 mol% TiO_2 it was negative. The γ_T of all the glasses in the present work was negative due to the negative temperature coefficient of linear refractive index (dn/dT), and decreased with increasing TiO_2 content, and was considered to be dominated by the two-photon absorption. For Ti^{3+}-containing $50Li_2O \cdot 15TiO_2 \cdot 35P_2O_5$ glass with negative γ_Z (-1.78×10^{-18} m^2W^{-1}), each of these three contributions was evaluated. The thermo-optic γ_T was determined to be -22.11×10^{-18} m^2W^{-1}, the optical Kerr γ_K was positive (11.87×10^{-18} m^2W^{-1}), and the resonant γ_R was positive (8.46×10^{-18} m^2W^{-1}).

Second Harmonic Generation from $YAl_3(BO_3)_4$-Containing Glass-Ceramics Prepared by Thermal Poling of Y_2O_3-Al_2O_3-B_2O_3 Glasses, Yoshitsugu YAMAMOTO, Tadanori HASHIMOTO, Hiroyuki NASU and Kanichi KAMIYA: Jpn. J. Appl. Phys., 42, pp. 5043-5047, 2003.

Transparent glass-ceramics containg $YAl_3(BO_3)_4$ crystals were prepared by thermal poling of the Y_2O_3-Al_2O_3-B_2O_3 glasses. Second harmonic generation coluld be measured from both the glass-ceramics prepared with/without applied voltage, however, intensity is markedly enhanced in the samples prepared with applied voltage. In the thermally poled samples, the preferred orientaion of precipitated $YAl_3(BO_3)_4$ crystals was observed, which may be attributed to the enhancement of second harmonic intensity.

The Influence of Matrix on Quantum Size Confinement of Semiconductor Microcrystals Doped in Glass Thin Films Prepared by RF-Sputtering, Hiroyuki NASU, Hiroshi IWATANI, Takafumi IWANO, Tadanori HASHIMOTO and Kanichi KAMIYA: Jpn. J. Appl. Phys., 42, pp. 270-273, 2003.

Various types of semiconductor microcrystal-doped glass thin films were successfully prepared by RF-sputtering. The blue shift of the absorption edge in the visible light region, caused by the quantum confinement effect, was observed in all the thin films. The amount of the blue shift was found to depend significantly not only on the types of semiconductor dopants and the microcrystal radius but also on the type of matrix. The blue shift of semiconductor microcrystals with a small exciton Bohr radius, such as CuCl, showed an exciton confinement effect. On the other hand, the blue shift of microcrystals with a large Bohr radius, such as CdSe, has been expected to follow the electron-hole independent confinement model. But it was found to deviate significantly from the theoretical curve. This deviation was explained in terms of the Coulomb interaction between electron and hole, size-dependent dielectric constants of the dopants and the dielectric constant of matrix.

Development of Nonlinear Optical Materials Dispersed with Ultra-Fine Silver Particles [in Japanese], Noritsugu HASHIMOTO, Tadanori HASHIMOTO, Hiroyuki NASU and Kanichi KAMIYA: Reports of the Mie Prefectural Science and Technology Promotion Center Industrial Research Division, 27, pp. 71-76, 2003.

Ag aerosol particles generated by the evaporation-condensation method were deposited on a glass substrate. Thin film thus obtained consists of nano-sized Ag particles. Absorption spectrum shows a peak due to surface plasmon resonance, and absorption peak wavelength of as-deposited samples was shifted toward longer wavelength with increasing particle diameter. In the case of annealed samples, absorption peak wavelength was much shorter than that of as-deposited samples. Nonlinear refractive index and nonlinear absorption coefficient determined by Z-scan technique were negative, and its absolute value for as-deposited samples was increased as the absorption peak wavelength became close to the laser wavelength used in the measurement. Nonlinear refractive index for annealed sample was increased with decreasing particle diameter due to quantum confinement effects.

Glucose Degradation Products (GDP) Retard Remesothelialization Independently of D-Glucose Concentration, Llinos W MORGAN*, Anders WIESLANDER*, Malcolm DAVIES*, Takashi HORIUCHI, Yuji OHTA*, M Janine BEAVIS*, Kathryn J. CRAIG*, John D. WILLIAMS* and Nicholas TOPLEY*: Kidney Int., 64, pp.1854-1866, 2003.

To examine the effects of specific GDP on the remesothelialization process, the impact of conventional and low GDP peritoneal dialysis solutions, D-glucose, and individual GDP in a scratch-wounding model was assessed. In untreated HPMC, the rate of wound closure was linear and the process was complete by 18 +- 3.6 hours(N=16). In wounded HPMC exposed to dilutions of heat-sterilized but not filtered laboratory solutions (1.5% or 4.0% glucose,pH7.4), remesothelialization was significantly retarded (P=0.04 and P=0.009 vs. M199, respectively). In Gambrosol, remesothelialization was significantly retarded in both 1.5% and 4.0% solutions. Remesothelialization was dose-dependently retarded in HPMC exposed to 3,4-DGE (>10 μ mol/L), formaldehyde (>5 μ mol/L) but not by exposure to the other GDP tested even at 5 times the concentration present in low glucose solutions. These data identify that the formaldehyde and 3,4-DGE present in heat-sterilized peritoneal dialysis solutions are important in reducing mesothelial cell regeneration. Specifically targeting their removal may have major benefits in preserving the mesothelium during long-term peritoneal dialysis.

Image Analysis of Remesothelialization Following Chemical Wounding of Cultured Human Peritoneal Mesothelial Cells: The Role of Hyaluronan Synthesis, Takashi HORIUCHI, Keiichi MIYAMOTO, Sunao MIYAMOTO*, Mika FUJITA*, Nami SANO*, Kyoko MINAMIYAMA*, Yuichirou FUJIMURA*, Koichi NAGASAWA*, Chie OTSUKA* and Yuji OHTA*: Kidney Int., 64, pp.2280-2290, 2003.

To understand what happens during the wound healing process of the mesothelium, we have developed an in vitro wounding model of cultured human peritoneal mesothelial cells (HPMCs) utilizing an image acquisition and analysis system. Using this system, cell mobility and hyaluronan synthesis were quantified and their interrelationship discussed. Centripetal migration of the HPMCs into the wound area was the predominant process involved in wound repair with proliferation playing a secondary role. Staining for B-HABP was confined to the remesothelialized area when wound closure was complete at 24 hours. At 48 hours after wound closure, the stained area was even more visible, although somewhat diffuse; thereafter, staining was reduced to almost background levels. The cell culture model of wound healing used in our study has enabled us to demonstrate quantitative image data of the cellular processes that occur during wound healing. Synthesis and subsequent decomposition of hyaluronan appears to be related to the mobility of the wounded and intact HPMCs in this model system.

Expression of mRNA for Growth Factors and Extracellular Matrix Proteins after Injury to Cultured Peritoneal Cells: Does the Healing Process Contribute to Peritoneal Ultrastructural Alteration?, Takashi HORIUCHI, Koki FUJIKAWA*, Kimio TAKAI*, Akinobu SUGA*, Katsusuke NAITO*, Atsushi OHATA*, Shinya NAKASONE*: J. Artif. Organs, 6, pp. 253-259, 2003.

To test a possible mechanism for peritoneal membrane alteration, we investigated whether chemically injured peritoneal mesothelial cells and fibroblasts upregulate their production of growth factors and ECM as a consequence of the healing process. A significant increase was only observed for TGF-β1, while VEGF showed the least change with time. For RPFB, HGF, b-FGF, VEGF, and FN mRNA expression were slightly suppressed compared to control levels up to 72h postwounding. TGF-β1, however, increased markedly above control expression levels by the end of the wound healing process. The production of profibrotic growth factors by mesothelial cells in response to injury may represent a mechanism whereby fibroblast activation, resulting in fibroblast hyperplasia and excessive extracellular matrix accumulation, culminates in alteration of the peritoneal membrane ultrastructure.

Inhibition of Cryogelation by the Novel Synthetic Peptide (Gly-Arg-Lys-Lys-Thr): Recognition Site of Extra Domain A Containing Fibronectin for Heparin in Cryogelation, Keiichi MIYAMOTO, Daisuke KOBAYASHI, Rizu MAEDA, Takaharu ITO, Takashi KOMAI: Int. J. Biol. Macromol. 31, pp. 207-15, 2003.

Cryogel is a physical gel formed by the heterophilic aggregation of extra domain A (EDA) containing fibronectin [EDA(+)FN], plasma fibronectin (pFN), fibrinogen (Fbg) and heparin (Hep) in the blood of rheumatoid arthritis (RA) patients. In cryogelation EDA(+)FN cross-links to form an interaggregate of cryogel with Hep. In the present study, we determined the recognition structure of Hep for EDA(+)FN by using oligo- and desulfonated-Hep. We also determined the recognition structure of EDA(+)FN for Hep by an inhibition experiment on the heparin binding domain II (HepII) in EDA(+)FN with the synthetic peptides, Arg-Arg-Ala-Arg (RRAR), Asp-Gln-Ala-Arg (DNAR), Ile-Lys-Tyr-Glu-Lys (IKYEK), and Gly-Arg-Lys-Lys-Try (GRKKT). The GRKKT sequence clearly inhibited bonding between EDA(+)FN and Heps containing oligo- and desulfonated-Hep. These results demonstrated that inhibition of cryogelation in plasma could progress to a novel treatment for RA.

Preparation of Polyion Complex Capsule and Fiber of Chitosan and Gellan-Sulfate at Aqueous Interface, Hiroyuki YAMAMOTO*, Kousaku OHKAWA*, Emi NAKAMURA*, Keiichi MIYAMOTO, Takashi KOMAI: Bull. Chem. Soc. Jpn., 76, pp. 2053-2057, 2003.

The electrostatic interaction between polysaccharides has been studied. Different characteristic surface structures, such as true spheres and fibrous forms, are made front gellan-sulfate (GS) and chitosan via polyion complex (PIC) formation. When a chitosan solution is added dropwise into a GS solution, spherical droplets form in the GS solution. The procedure makes true spherical capsules with various diameters, which are stable enough for finger pinching or magnetic stirring in distilled water. The soft droplet capsule is acid resistant, alkali resistant, and stable in boiling water. When an aqueous GS solution is added into an aqueous chitosan solution without mixing, a film of PIC is formed at the interface. When this PIC film is withdrawn from the interface, a fiber line forms in the wet states. After the intact wet fiber is dried in air, a strong fiber forms. The tensile strength of the strongest fiber created is 196 MPa.

Release of (1 → 3)- β -D-Glucan from Depth-type Membrane Filters and Their In Vitro Effects on Proinflammatory Cytokine Production, Takashi HORIUCHI, Atsushi OHATA*, Makoto USAMI*, Koichi NAGASAWA*, Keiko KINOSHITA*: Artificial Organs, 27(8), pp.728-735, 2003.

To clarify the origin of (1→3)- β -D-glucan in blood products and assess the biological activity of filter extracts, we evaluated (1→3)- β -D-glucan extraction from depth filters used to process blood products and their in vitro effects on proinflammatory cytokine production from macrophages. Cellulose or nylon filters were analyzed for (1→3)- β -D-glucan using the Fungitec G test. To evaluate the biological activity of the filter extracts, Mono Mac 6 cells (a human macrophage cell line) were cultured with filter extracts with or without lipopolysaccharide, and tumor necrosis factor-alpha (TNF- α) and interleukin-1 beta (IL-1 β) concentrations in the culture media were measured. (1→3)- β -D-glucan was released from seven cellulose filters but the nylon filter level was undetectable. Proinflammatory cytokine production ranged from 74.3% to 119.0% of the control for TNF- α and 81.2% to 115.9% for IL-1 β . TNF- α and IL-1 β levels were low without lipopolysaccharide. The data indicate that (1→3)- β -D-glucan in blood products is contaminated with the depth filters and that these filter extracts modulate proinflammatory cytokine production from macrophages.

Experimental Proof of Contamination of Blood Components by (1→3)- β -D-Glucan Caused by Filtration with Cellulose Filters in the Manufacturing Process, Takashi HORIUCHI, Koichi NAGASAWA*, Tatsuyuki YANO*, Go KITABAYASHI*, Hiroaki MORIMOTO*, Yuji YAMADA*, Atsushi OHATA*, Makoto USAMI*: J. Artif. Organs, 6, pp. 49-54, 2003.

To investigate the contamination of blood components by (1→3)- β -D-glucan from cellulose filters, in vitro experiments were performed by using six cellulose filters and a nylon filter. Human serum albumin (HSA) solution (100ml) was flowed through each filter after rinsing with 100ml of distilled water, and (1→3)- β -D-glucan in each fraction was determined by Fungitec G test MK. The concentration of (1→3)- β -D-glucan eluted from cellulose filter in 100-ml distilled water fractions ranged from 6 to 207pg/ml, and that of HSA fractions ranged from 33 to 20,784pg/ml. These date showed that remarkably higher (1→3)- β -D-glucan levels were detected in HSA fractions flowed through cellulose filter in spite of advance rinsing with 100ml of distilled water. In the case if a nylon filter, (1→3)- β -D-glucan was not eluted in either fraction. These results indicate that (1→3)- β -D-glucan contamination in blood components is caused by filtration with cellulose filters in the manufacturing process.