
Hyperbranched polymer (poly-1a) with sulfonic acid groups at the end of chains was successfully synthesized. Interpenetration reaction of poly-1a with a hyperbranched polymer with acryloyl groups at the end of chains (poly-1b) as a cross-linker afforded a tough electrolyte membrane. The poly-1a and the resulting electrolyte membrane showed the ionic conductivities of \(7 \times 10^{-4}\) and \(8 \times 10^{-5}\) S/cm, respectively, at 150 °C under dry condition. The ionic conductivities of the poly-1a and the electrolyte membrane exhibited the VTF type temperature dependence. And also, both poly-1a and the resulting electrolyte membrane were thermally stable up to 200 °C.


New comblike polymers such as a homopolymer (poly-4) of 3,5-bis[poly(ethylene glycol) methyl ether (350, n=7.2)]styrene (4) and an alternating copolymer (poly-4/TCNQ) of 4 with 7,7,8,8-tetracyanoquinodimethane (TCNQ) were prepared as a plasticizer for the poly(ethylene oxide) (PEO)-LiN(CF₃SO₂)₂ electrolyte, and the ionic conductivities, thermal property, electrochemical and thermal stabilities, and mechanical property for the comblike-based polymer electrolytes, composed of the comblike polymers, poly(ethylene oxide) (PEO), and LiN(CF₃SO₂)₂, were investigated. The polymer electrolytes containing an alternating copolymer poly-4/TCNQ showed the higher ionic conductivity, better thermal stability and better mechanical stability than that containing a homopolymer poly-4, due to the presence of an aromatic ring and a polar cyano group of the TCNQ unit.

Solid Polymer Electrolytes Based on Poly(1,3-diacetyl-4-imidazolin-2-one), Hiroyuki MITSUDA, Takahiro UNO, Masataka KUBO, Takahito ITOH: Polymer Bulletin 57, pp. 313-319, 2006

Solid polymer electrolytes composed of a homopolymer (poly(AcIM)) of 1,3-diacetyl-1,4-imidazolin-2-one (AcIM) and lithium bis(trifluoromethanesulfonimide) (LiTFSI) or of copolymers (poly(AcIM/VC)) of AcIM with vinylene carbonate (VC) and LiTFSI were prepared and their ionic conductivities and thermal properties were investigated. For the polymer electrolyte of the poly(AcIM) with LiTFSI, the highest ionic conductivity was found at the [Li]/[O] ratio of 1/3 with the values of \(8.5 \times 10^{-5}\) S/cm at 80 °C and \(1.7 \times 10^{-6}\) S/cm at 30 °C, respectively. In the polymer electrolyte of poly(AcIM/VC) with LiTFSI at the [Li]/[O] ratio of 1/3, the ionic conductivity increased with increasing VC unit content in the copolymers, and the highest ionic conductivity was found at the AcIM/VC ratio of 39/61 (mol%) with the values of \(7.0 \times 10^{-4}\) S/cm at 80 °C and \(6.7 \times 10^{-5}\) S/cm at 30 °C, respectively. This copolymer electrolyte showed a linear relationship between the ionic conductivity and the reciprocal of the temperature, indicative of the system decoupled from the segmental motion of the polymer.

Synergistic effect of red phosphorus, novolac and melamine ternary combination on flame retardancy of
New flame retardant system for poly(oxymethylene) (POM) has been studied. The combination of red phosphorus with novolac and melamine was found to act as an effective flame retardant of POM. The base POM exhibited very low limiting oxygen index (LOI) value of 15.3, while the flame retarded POM gave remarkably high LOI value of 37.5 and UL94 V-1 ranking without dripping at 0.8 mm thickness. The results of cone calorimetry, thermogravimetry and FTIR analysis suggested that the flame retarding mechanism is the intumescent char formation in the condensed phase. Novolac having a phenolic hydroxyl group is miscible with POM, and in the flaming process, red phosphorus yields phosphine and its acidic product such as phosphoric acid due to hydrolysis and oxidation reactions. In addition, all of novolac, melamine and phosphine are able to readily react with formaldehyde generating from POM during burning to give the reinforced and cross-linked char network through the polyaddition and polycondensation reactions. Therefore, the red phosphorus/novolac/melamine ternary combination system could synergistically promote the high flame retardancy of POM without the flaming drips.

Topochemically controlled [2 + 2] photocycloaddition took place at the quinonid double bond of the 7-bromoethoxycarbonyl-7-cyano-1,4-benzoquinone methide (1) to afford its cyclobutane dimer.

Two different molecular weight hyperbranched polymers (HBP-PA(L) and HBP-PA(H)) with phosphonic acid groups at the chain ends were successfully synthesized. The ionic conductivities of the low molecular weight HBP-PA(L) and the high molecular weight HBP-PA(H) were found to be 1.3x10^{-4} and 6.4x10^{-5} S/cm, respectively, at 135 °C under dry condition, and showed the VTF type temperature dependence. And also, both polymers were thermally stable up to 300 °C, and they had suitable thermal stability as an electrolyte in the polymer electrolyte fuel cell operating under dry condition.

Red, green and blue fluorescent poly(arylene vinylene)s were prepared by Wittig reaction. Polycondensation of tetraethoxysilane (TEOS) was carried out in the presence of a mixed solution of these polymers to give a silica hybrid in which RBG fluorescent polymers were immobilized without phase separation. White light emission was observed from the ternary polymer blend/silica hybrid.


Titanium Tetraiodide Mediated Reductive Opening of Aziridines, Leading to the Aldol and Mannich-Type Reactions, Makoto SHIMIZU, Hiroshi KUROKAWA, Shuji NISHIURA, Iwao HACHIYA: Heterocycles, 70 (1), pp. 57-64, 2006


Ring Expansion Reaction of Cyclic \(\alpha\)-Keto Esters or \(\alpha\)-Cyano Ketones via Conjugate Addition to Alkynyl Imines: The Synthesis of Functionalized Medium-Sized Carbocycles, Iwao HACHIYA, Wataru MAEHARA, Yasushi YAMADA, Toru KAMIKI, Makoto SHIMIZU: Synlett, (19), pp. 3271-3274, 2006


Synthesis of Bicyclic Compounds Containing a 2-Pyridone Structure by Addition of Malonic Esters to


Geometries and electronic structures of the quintet and septet states of the [Mn(P)(O2)]− (P: porphinato) anion were theoretically investigated. Four local minimum geometries with two side-on additions of O2 to MnP, 1 (5B2) and 3 (7A2); and two end-on additions of O2, 2 (5A′) and 4 (5A′), were found. One of the side-on forms, 1, corresponds to that observed by X-ray crystallographic study. 3 is a septet state with higher spin than the quintet states of 1, 2, and 4. Each of the two end-on forms has the corresponding transition state with the side-on geometry. Energy differences among 1, 2, and 3 are less than 1 kcal mol−1. The electronic structures of four local minimum states were essentially different. 1 has an electronic structure presented as [MnII(O2−)]−. 2 has antiferromagnetically coupled diradical character presented by the formal chemical formula of [MnII•(O2•−)]−. 3 has ferromagnetically coupled diradical character. 4 is presented by [MnII(O2−)]−.


We have previously proposed the O2 reduction mechanism that the protons transfer from the K–channel to the active site of CcO. The second proton transfer to the hydroperoxy intermediate FeOOH did not lead the OO bond cleavage. It has been recently reported that the addition of the proton induces the OO bond cleavage to yield the productive H2O molecule and the oxo intermediate Fe=O, being inconsistent with our results. We have started this
A study to confirm whether the OO bond cleavage occurs or not upon the proton addition. We concentrated our study to the changes of the electronic structures of the heme a3 part throughout the sequential additions of the protons and an electron during the process of the O2 reduction. We employed a model that is composed of porphyrin without any substituents, Fe, and an imidazole as His376. We added sequentially protons and an electron to the heme(Fe)-dioxygen complex. The geometrical parameters were fully optimized without any constraints. The unrestricted hybrid exchange-correlation functional B3LYP method was used. The Wachters double zeta basis set was employed for Fe atom. The 6–31G* basis set was used for C, N, and H atoms, and the 6–311+G* for O atom. All calculations were carried out using the program package Gaussian 98. The proton addition to FeOO (H2) to yield FeOOH (H3) causes the electron transfer from the porphyrin ring to FeOOH moiety, giving the porphyrin–radical cation. The additional proton to FeOOH (H4) leads to the OO bond cleavage, yielding the hydrogen bonded complex of an oxo heme (compound I) and a H2O molecule. The bonding characters of FeOOH in H3 and H4 are identical, even though the electronic structures of the porphyrin rings in H3 and H4 are different. However, the proton addition to FeOOH (H3) does not lead to the OO bond cleavage. The protonated heme(Fe)-dioxygen complexes are effective models to investigate the reduction mechanism of an O2 molecule in CcO.


We made a theoretical study of the proton transfer path from C6H5+(H2O)4 to C6H5(H2O)4H+ with a planar cyclic geometry of (H2O)4H+ by the hybrid density functional B3LYP method. The proton transfer proceeds in a three-step manner. In the first step, the proton in C6H5+(H2O)4 moves from the terminal H2O molecule in the (H2O)4 cluster to yield a (H2O)3H+ cluster. In the last third step, one H2O molecule leaves from C6H5(H2O)4H+ to yield a C6H5(H2O)3H+ complex through the H-abstraction by the OH radical. It is found that the proton transfer and redistribution from p to r of the radical electron proceed separately.


The novel example of a vinylic hydrogen more reactive than a benzylic hydrogen was found by treatment of a twisted styrene derivative with a strong base followed by D2O quenching. In this paper, the full details of the examples of the highly activated vinyl hydrogens in twisted styrene derivatives are described, with a discussion on the correlation between the reactivity of the vinyl hydrogens and the magnitude of the twist. The highly reactive vinyl hydrogens could be rationalized by considering the novel orbital interaction between the * orbital of the benzene ring and the orbital of the vinylic C–H bond in the twisted styrene derivatives.


We report the geometrical features and electronic structures of di-oxo-bridged Mn–Mn binuclear complexes with H2O ligands [Mn2O2(H2O)8]9+ in the iso- and mixed-valence oxidation states. All of the combinations among Mn(II), Mn(III), and Mn(IV) ions are considered the oxidation states of the Mn–Mn center, and the changes in molecular structure induced by the different electron configurations of Mn-based orbitals are investigated in relation to
the oxygen-evolving complex (OEC) of photosystem II. The stable geometries of complexes are determined by using the hybrid-type density functional theory for both of the highest- and lowest-spin couplings between Mn sites, and the lowest-spin-coupled states are energetically more favorable than the highest-spin-coupled states except in the case of the complexes with the Mn(II) ion. The coordination positions of H$_2$O ligands at the Mn(II) site tend to shift from the octahedral positions in contrast to those at the Mn(III) and Mn(IV) sites. The shape of the Mn$_2$O$_2$ core and the distances between the Mn ions and the H$_2$O ligands vary depending on the electron occupations of the octahedral eg orbitals on the Mn site with an antibonding nature for the Mn–ligand interactions, indicating the trend as Mn(II)–O > Mn(III)–O and Mn(IV)–O, O–Mn(II)–O > O–Mn(III)–O > O–Mn(IV)–O among the iso-valence Mn$_2$O$_2$ cores, and O–Mn(lower)–O < O–Mn(higher)–O within the mixed-valence Mn$_2$O$_2$ core, and as Mn(II)–OH$_2$ and Mn(III)–OH$_2$ > Mn(IV)–OH$_2$ for the axial H$_2$O ligand. The optimized geometries of model complexes are compared with the X-ray structure of the OEC, and it is suggested that the cubanelike Mn cluster of the active site may not contain a Mn(II) ion. The effective exchange integrals are estimated by applying the approximate spin projection to clarify the magnetic coupling between Mn sites, and the superexchange pathways through the di-μ-oxo bridge are examined on the basis of the singly occupied magnetic orbitals derived from the singlet-coupled natural orbitals in the broken-symmetry state. The comparisons of the calculated results between [Mn$_2$O$_2$(H$_2$O)$_8$]$^{2+}$ in this study and [Mn$_2$O$_2$(NH$_3$)$_8$]$^{2+}$ reported by McGrady et al. suggest that the symmetric pathways are dominant to the exchange coupling constant, and the crossed pathway would be less important for the former than it would for the latter in the Mn(III)–Mn(III), Mn(IV)–Mn(IV), and Mn(III)–Mn(IV) oxidation states.


Epitaxial films of the perovskite, La$_{0.8}$Sr$_{0.2}$CoO$_3$ (LSC), for SOFCs cathode were deposited on yttria-stabilized zirconia (YSZ) single crystals by pulsed laser deposition method. The films were characterized by thin-film X-ray diffraction measurement, atomic force microscopy (AFM), transmission electron microscope (TEM), and ac impedance spectroscopy. The film orientations depend on the substrate planes. The LSC films on the YSZ (100) and (111) substrates showed the (110) orientation with different twin structures, while those on the YSZ (110) had (100) and (112) orientations. Surface morphology of the films also depends on the substrate orientations. These films showed different electrode properties depending on the orientations. The relationships between the properties, the film orientations, surface morphology, and lattice misfit are discussed.

An anomalous thermal expansion in the perovskite system, Gd$_{1-x}$Sr$_x$MnO$_3$ (0 ≤ x ≤ 0.3), A. Hirano, F. Hirano, T. Matsumura, N. Imanishi and Y. Takeda : Solid State Ionics 177, pp. 749-755, 2006

The thermal expansion behavior of sintered samples of Gd$_{1-x}$Sr$_x$MnO$_3$ (X=0.0–0.4) was studied. The sintered bodies in this system showed negative thermal expansion over a wide temperature range. The detailed crystal structure refinements with respect to temperature showed that the volume of the orthorhombic perovskite lattice monotonically increased with temperature, however, in addition to this, the release of distortion from the Jahn-Teller effect of Mn$^{3+}$ ion occurred over a wide temperature range, which brought the negative expansion of the $a$- axis, although the $b$- and $c$-axes increased with temperature. The anomalous thermal expansion is explained by the sum of the effects of the shrinkage of the $a$-axis and absorption of the $b$- and $c$-axes' expansion by the pores in the sintered body.

Solid solution materials of Li$_2$CuO$_2$ and Li$_2$NiO$_2$ were studied with respect to their electrochemical performance and crystal structure. The Li$_2$CuO$_2$–Li$_2$NiO$_2$ system shows a solid solution over the whole composition range with the orthorhombic structure. Pure Li$_2$CuO$_2$ has a reversible capacity of only 100 mA h/g, and the capacity of Li$_2$Cu$_{1-x}$Ni$_x$O$_2$ increased with increasing the content of Ni. The maximum capacity of 250 mA h/g is obtained for Li$_2$Cu$_{0.5}$Ni$_{0.5}$O$_2$, and it exhibits a good reversibility for charge and discharge cycles. The orthorhombic Li$_2$CuO$_2$ undergoes a phase change to the monoclinic LiCuO$_2$ during lithium deintercalation, while nickel-rich compositions show a new phase that is different from either the original orthorhombic or monoclinic structure.

Impedance study and TEM characterization of a PLD perovskite air electrode, Nobuyuki Imanishi, Yoshiaki Sumiya, Ken Yoshimura, Tadaaki Matsumura, Atsushi Hirano, Yasuo Takeda, Daisuke Mori* and Ryoji Kanno* : Solid State Ionics 177, pp. 2165-2173, 2006

TEM observation and electron diffraction analysis of a laser ablation perovskite film was carried out. The film was deposited on a single-crystal substrate and showed epitaxial growth normal to the substrate. The crystal orientation of the perovskite film varies depending on the kind of single-crystal substrate. The surface structure of the atomic arrangement was investigated based on an analysis of electron diffraction patterns. Its relation to the kinetics of the reduction of molecular oxygen is discussed.


Lithium-transition-metal nitrides are promising anode candidates for Li-ion batteries. However, lithium must be extracted from the nitrides in an initial anodic oxidation, indicating these compounds cannot directly combine with the current cathodes to constitute cells. This deterrent can be overcome by introducing a certain amount of Co$_3$O$_4$, which shows large capacities and relatively high oxidation/reduction potentials, into the electrodes containing the above nitrides. A thermodynamically spontaneous reaction between these two active hosts results in a delithiated state of lithium metal nitrides. Under cycling within 1.4–0 V vs Li/Li$^+$, Co$_3$O$_4$ is relatively inert to lithium and the nitrides become electrochemically active. The composite electrodes show high first-cycle efficiency of 100%, large capacities of 500 mAh g$^{-1}$, and excellent cyclability. Furthermore, research revealed that the composite electrodes demonstrated high cycling stability operating with polyethylene oxide (PEO) electrolytes at the elevated temperature. The reaction heating of the composite electrode under high Li utilization with PEO electrolytes via differential scanning calorimetry measurement was found to be extremely low compared with those of the lithium metal and the Li-alloy-based systems, suggesting that the composite electrodes could be promising anode candidates for all-solid-state PEO Li-ion batteries in terms of capacity, first-cycle charge efficiency, and thermal reliance.

Na$_x$FeO$_2$ was obtained by chemical oxidization method using NO$_2$BF$_4$ and Br$_2$ which shows the redox potential of ca. 5.1 V and ca. 4.1 V vs Li$^+$/Li$^-$, respectively. The oxidized products showed different X-ray diffraction patterns depending on the oxidizing species. In case of NO$_2$BF$_4$, as soaking time progressed, new phase increased with decreasing of NaFeO$_2$ as stating material. The oxidized Na$_x$FeO$_2$ was possible to be inserted the Li ion electrochemically, and resulted in the crystal structure similar to the layered LiFeO$_2$ synthesized by the Li-ion-exchange method from NaFeO$_2$. Reversible discharge-charge reactions were progressed for Na$_x$FeO$_2$//Li cell, and ac.150 – 200 mAh/g of initial capacities were achieved although the capacities decreased with cycle numbers.


Degradation of Polychlorinated Dibenzo-p-dioxins in Aqueous Solution by Fe(II)/H₂O₂/UV System, Hideyuki KATSUMATA, Satoshi KANECO, Tohru SUZUKI, Kiyohisa OHTA, Yoshihiro YOBIKO*: Chemosphere, 63, pp. 592–599, 2006


Cycle Performance of Sol-Gel Optical Sensor Based on Localized Surface Plasmon Resonance of Silver Particles, Noritsugu HASHIMOTO, Tadanori HASHIMOTO, Taichi TERANISHI, Hiroyuki NASU and Kanichi KAMIYA:


An image analysis algorithm for kinematics and morphology measurement of cells for the evaluation of tissue construction, Tomoko GESSEI, Chie OTSUKA, Masatoshi BANNO, Keiichi MIYAMOTO, Yuji OHTA, Takashi HORIUCHI: IFMBE Proceedings, 14:2006