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Quaterthiophenediphosphonic acid (QDP): A Rigid, Electron-Rich Building Block for Zirconium-Based Multilayers

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The title compound, synthesized in three steps from 2,2′-bithiophene, was deposited alternately with tetravalent zirconium as a multilayer on phosphorylated substrates. This is the first example of zirconium phosphonate multilayer formation with either a nonaliphatic or a rigid diphosphonic acid. Procedures were devised for (3-aminopropyl)silylating, phosphorylating, and zirconating silicon oxide surfaces. Deposition of QDP onto these surfaces proceeded best from DMSO solution at 80 °C. Ellipsometry, UV absorbance, and X-ray fluorescence were consistent with formation of densely packed films. The films were insulating and were unresponsive to I_2 vapor, whereas Br_2 caused reversible surface doping. We hope to employ QDP as an electron-donating element in heterogeneous multilayers based on the zirconium phosphonate deposition strategy.

Introduction

Organic thin films may be employed in a variety of ways as either "passive" layers, providing electrical or environmental isolation[1] or substrate planarization,[2] or as "active" layers, offering photoconductivity and photovoltage,[3] electrochromism,[4] rectification,[5] tunable dielectric response,[6] or nonlinear optical susceptibility.[7] These properties are best attained in materials that are densely packed and have controlled dimensions and architectures. In particular, the directional sequence or orientation of the chemical components, upon which many of the active responses are critically dependent, can be dictated by depositing a film layer by layer, for which several techniques have been considered. For example, one strategy is to spin-coat or electrochemically grow polymers with different electronic properties sequentially on a substrate, as has been done with pairs of polyacetylenes[8] or polyheterocycles.[9] Another possibility is the sequential sublimation of solids with different bandgaps onto substrates.[10] The Langmuir–Blodgett (LB) method has become popular for fabricating heterogeneous molecular assemblies and assemblies of monolayers with polar order.[11] Polarization or excitation of these assemblies results in fluorescence, diode activity, and highly anisotropic conductivity and capacitance. All of these materials are usually held together largely by dispersive interactions, and lack the strength and temperature stability associated with more robust materials such as inorganic crystals, ceramics, and high-performance polymers.

The report of the layer-by-layer deposition of zirconium 1,10-decanediylbisphosphonate, $Zr(O_3P(CH_2)_{10}PO_3)$, by Mallouk and co-workers[12a,b] initiated the development of a new and potentially important strategy for the deposition of thin-film coatings. Knowing that organic phosphonic acids and phosphoric acid itself form highly insoluble, layered salts with Zr(IV) and other transition-metal ions,[13] Mallouk and co-workers showed that Zr(IV) and the bisphosphonic acid could be alternately adsorbed on a substrate to form analogous materials one layer at a time. Because they are held together by strong ionic and coordinative interactions, the zirconium phosphonate multilayers are highly resistant to thermal, mechanical, and chemical stress. In principle, this strategy offers a means of incorporating various other organic moieties in directional,[12c] highly ordered, high-strength films. Although a great variety of organics, including polymer and oxidizable compounds, have been intercalated into other inorganic layered materials,[14] no protocol for layer-by-layer buildup has been proposed for them.

Our objective is to synthesize layering components for the assembly of heterogeneous multilayers with electronic, mechanical, and chemical properties that are not necessarily obtainable from homogeneous materials. An additional goal is the development of very thin, defect-free barrier layers for use as dielectrics or protective coatings. As a first step, we examine quaterthiophenediphosphonic acid (QDP), a rigid diphosphonic acid with an electron-rich core, for multilayers assembled by using the zirconium phosphonate strategy.

An oligothiophene was selected for the core because of both structural and electronic considerations. Crystal structures of bi- and terthiophene indicate that these

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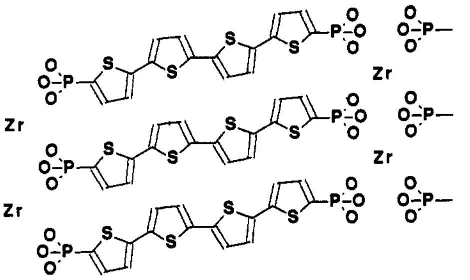


Figure 1. Zr–QDP multilayer geometry. The C5–C5′ (C2″–C5‴) distance, projected on a line parallel to the C–P bonds (normal to the layers) is 6 Å,[15] the C5′–C2″ bond length is ca 1.45 Å,[15] and the distance from C5 (C5‴) to the Zr layer is ca 3.75 Å.[13] From these values, a span of 21 Å is predicted between Zr layers.

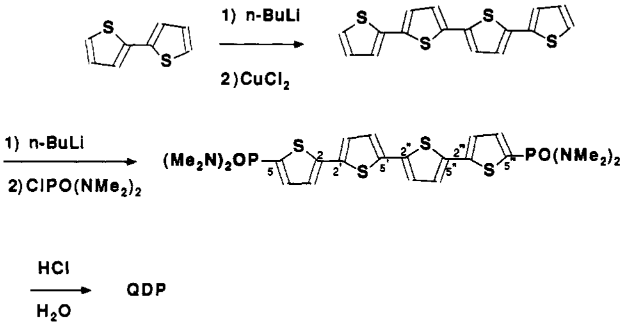
species are nearly planar, rigid bars in the solid state,[15] and experience with LB films has shown that oligothiophenes pack well as monolayers.[16] Electron excitation and hole formation in thiophene oligomers has been observed in a variety of settings, including solutions,[17] crystalline solids,[18] LB films,[16a-d] and solid charge-transfer compounds,[19] and manifested in ESR signals,[17b-d] semiconduction,[16a-c,e,18] and nonlinear optical properties.[20] An additional attribute of oligothiophenes is that the highest occupied molecular orbitals extend to both ends of the molecule, which can possibly assist interlayer electron transfer. QDP, illustrated in Figure 1, contains enough thiophene residues to render it electron donating and suitable for rigid-bar packing. Two two C–P bonds are antiparallel and situated at either end of the molecule, an arrangement that accommodates the zirconium phosphonate multilayer structure in which the phosphonate groups are directed perpendicularly to the layer planes.

Here we report the synthesis of QDP, optimization of procedures for substrate preparation and compound deposition, and ellipsometric, spectroscopic, and X-ray fluorescence characterization of multilayers deposited on silica and glass. We also briefly describe the electrochemistry of a QDP derivative, deposition of QDP on other substrates, and interaction of the films with Br_2 and I_2 as oxidizing dopants. Our results indicate that QDP is indeed an excellent structural unit for multilayer formation using zirconium interlayers and reversibly forms a complex with adsorbed bromine.

Experimental Section

Synthesis of 2,2′:5′,2″:5″,2‴-Quaterthiophene-5,5‴-diylbis(phosphonic acid) (QDP). Tetrathiophene was prepared by treating 10.2 g of bithiophene (Aldrich) with 1 equiv of BuLi (Aldrich) in 300 mL of tetrahydrofuran (THF) at −70 °C for 15 min and then transferring the resulting mixture to a second flask containing a suspension of $CuCl_2$ in 60 mL of THF at −70 °C. The combined suspension was stirred overnight at ambient temperature, hydrolyzed with 5 mL of H_2O and 100 mL of 2% aqueous HCl, and filtered. The collected orange solids were washed with H_2O and dried; yield 5.2 g. This material (0.90 g, 2.7 mmol) was stirred in 280 mL of THF under Ar at −30 °C, and *n*-BuLi (8.8 mmol) was added. After 2 h at −30 °C, a solution of bis(dimethylamino)phosphorochloridate (Aldrich, 1.4 mL, 9.6 mmol) and 0.6 mmol of *n*-BuLi (to remove adventitious HCl) in 20 mL of THF was added. The solution was allowed to warm slowly to room temperature and was stirred for 3 days. The mixture was diluted with 100 mL each of Et_2O and H_2O. The aqueous layer was extracted with 50 mL of CH_2Cl_2, and the combined organics were dried with $MgSO_4$, filtered, and concentrated to 2.7 g of an oil. Chromatography on 60 g of alumina, eluting with 0.6% MeOH in EtOAc (700 mL in all) gave 0.81 g (50%) of a brilliant orange solid after concentration of the fraction containing the most polar of the three yellow components (mobile with MeOH–EtOAc but not with EtOAc alone) and crystallization from CH_2Cl_2–hexane. ^1H NMR ($CDCl_3$) δ 2.7 (d, 24, J = 17 Hz, Me), 7.09 and 7.13 (ab q, 4, J = 4 Hz, central ring H), 7.19 (d of d, 2, J_{HH} = 4 Hz, J_{PH} = 3 Hz, 3- and 3‴-H), 7.42 (d of d, 2, J_{HH} = 4 Hz, J_{PH} = 8 Hz, 4- and 4‴-H). An analytical sample was prepared by precipitation of a MeOH solution with H_2O and recrystallization from CH_2Cl_2–hexane. Anal. Calcd for $C_{24}H_{32}N_4O_2P_2S_4$: C, 48.14; H, 5.39; N, 9.36. Found: C, 47.73; H, 5.46; N, 9.01.

Scheme I



A portion of the above tetraamide (210 mg) was dissolved in 60 mL of dioxane at 80 °C. The temperature was allowed to cool to 35 °C, and 12 mL of H_2O and 18 mL of 12 N HCl were added. The suspension was stirred for 18 h at 35 °C, partially concentrated, and filtered. The yellow-brown solids (120 mg, 70%), suitable for deposition, contained pure QDP dihydrate; ^1H NMR (DMSO-d_6) δ 7.35–7.40 (m), ^{31}P NMR (DMSO-d_6) δ 4.8 (s). Anal. Calcd for $C_{16}H_{12}P_2S_4O_6{\cdot}2H_2O$: C, 36.50; H, 3.06; P, 11.77; S, 24.36. Found: C, 36.70; H, 2.80; P, 11.51; S, 24.52.

Substrate Preparation. Silicon wafers and the glass slides used in parallel depositions were cleaned with a solution of 3 volumes of H_2SO_4 and 1 volume of 30% H_2O_2 (*Caution!* This solution reacts violently with organic material!) for 10 min prior to priming the surfaces. Glass slides and ITO substrates (submicron ITO layers sputtered onto glass) processed together were cleaned with 2 N HCl for 5 min. Gold on silicon or mica substrates was primed by soaking the substrate in a 1.5 mM ethanolic solution of 8-mercaptooctylphosphonic acid for 3–7 days. The glass slides were treated with 1% (v/v) (3-aminopropyl)trimethoxysilane (Petrarch) in boiling anhydrous octane for 10 min, followed by phosphorylation (10 mM $POCl_3$ and 2,4,6-collidine in anhydrous acetonitrile) for 1.5–16 h at room temperature. The ITO substrate was phosphorylated directly without intermediate priming. At this point, all of these substrates were assumed to have a phosphonic acid surface that could then be zirconated (5 mM $ZrOCl_2$ (Alfa) in water) overnight at room temperature.

Multilayer Deposition. Multilayers were assembled by using a two-step deposition scheme. Substrates with a zirconated surface were placed in a solution of QDP acid (1 mM in 5% H_2O/DMSO, adjusted to pH 3 with HCl) for 20 min at 80 °C, rinsed in DMSO for 30 min at 80 °C, washed with ethanol, and spun dry. Treatment of the substrates with the $ZrOCl_2$ solution for 10 min at room temperature followed by an H_2O wash and spin drying completed the sequence. This procedure was repeated to obtain the desired number of layers. The ellipsometric and absorbance

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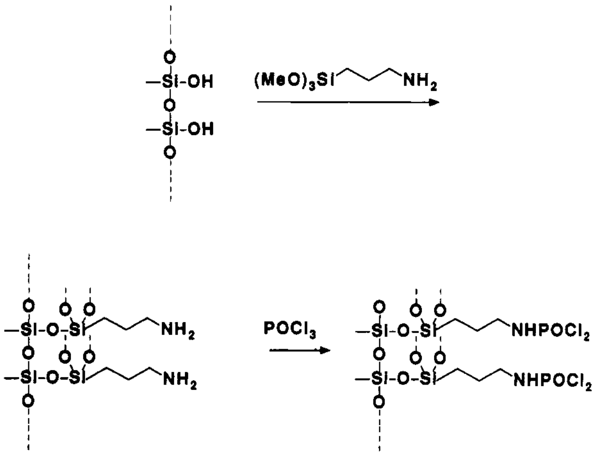
Scheme II



measurements were done on phosphonic acid terminated surfaces.

Results

Synthesis and Electrochemistry. QDP was synthesized according to Scheme I. The chlorophosphoric diamide electrophile had previously been substituted by carbon nucleophiles only in conjunction with enolate chemistry.[21] Using dilithiated terthiophene as a model, the diamide was more reactive and more selective than diphenyl phosphochloridate in forming the C–P bond and gave a tetraamide that was easily hydrolyzed to the free diphosphonic acid. The tetraamide of QDP displayed a nearly reversible electrochemical oxidation at 1.1 V vs SCE in 0.05 M Bu_4NPF_6 in THF, using a 1-mm Pt disk working electrode and a Pt wire counterelectrode. (Electrochemistry of TCNQ in this medium is fully reversible.) Unsubstituted quaterthiophene was oxidized irreversibly at a similar potential. QDP itself was insufficiently soluble in suitable electrochemical media to obtain voltammetric data.

Substrate Preparation and Priming. Because two of the most desirable substrates for growing multilayers, silicon wafers and glass slides, have Si oxide surfaces, we sought a reliable method for converting Si oxide surfaces to phosphate surfaces. Having found the previously reported[12a] techniques difficult to implement, we chose the priming sequence illustrated in Scheme II. A variety of media were examined for the (aminopropyl)silylation step, including the recommended[22] (aminopropyl)trimethoxysilane in aqueous EtOH, neat (aminopropyl)silane vapor at partial vacuum, the (aminopropyl)silane in anhydrous octane at reflux, and the vapor above the refluxing octane solution. The hot liquid octane solution provided the most reproducible coverages, usually tens of angstroms on Si wafers. Less useful coverages of <1 monolayer or >10 monolayers, occasionally observed in the other media, were avoided in the hot octane. The resulting aminated surface was phoshorylated with $POCl_3$ and a tertiary amine and then zirconated by aqueous $ZrOCl_2$.

QDP Deposition Conditions. Depositions of QDP on silicon were performed under a variety of conditions, some of which are listed in Table I. Judgements concerning the density of coverage in a particular trial were made assuming a theoretical upper limit of 21 Å, graphically derived in Figure 1, for the thickness of a Zr–QDP monolayer. The data are representative of those that led to the determination of deposition conditions for multilayer preparation. Aqueous dimethyl sulfoxide (DMSO) was chosen as the solvent because of the solubility of QDP in that medium, while EtOH, which has been employed in other zirconium phosphonate depositions, did not form stable solutions with QDP and was therefore not used. The kinetics of adsorption were greatly accelerated at higher temperatures, and adjustment of the pH to 3 apparently helped ensure complete coverage. The rate of zirconation of the phosphonate surfaces was nearly instantaneous, <5 min being sufficient to form a base for the succeeding organic layer.

Table I. Ellipsometric Thickness of Zr–QDP Monolayers on Phosphonylated Si Substrates[a]

T, °C	time	thickness,[b] Å	remarks
25	2 weeks	20	
25	5 h	14	
25	5 min	10	[QDP] = 2 mM, glass substrate, thickness by UV, pH = 3
60	24 h	21	50% DMSO:50% H_2O
60	10 min	10	50% DMSO:50% H_2O
80	20 h	12	
80	20 min	18[c]	pH adjusted to 3
80	5 min	20	[QDP] = 2 mM, pH = 3
80	30 min	14	saturated soln in EtOH
80	2 h	19	saturated soln in EtOH

[a] Deposition solution was 1 mM QDP in 95% DMSO:5% H_2O except as noted. [b] Including 1 layer of Zr. [c] Independent of zirconation time, 5 min–2 h.

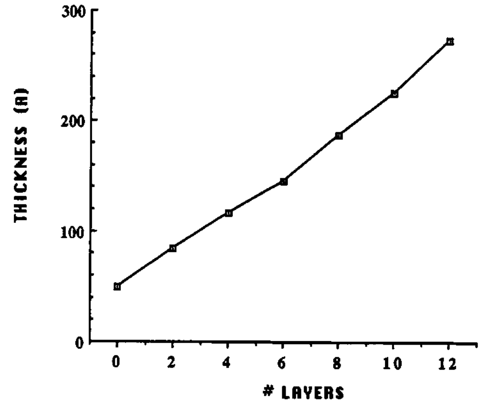


Figure 2. Ellipsometric thickness vs layer number for Zr–QDP on silicon, deposited as described in the Experimental Section.

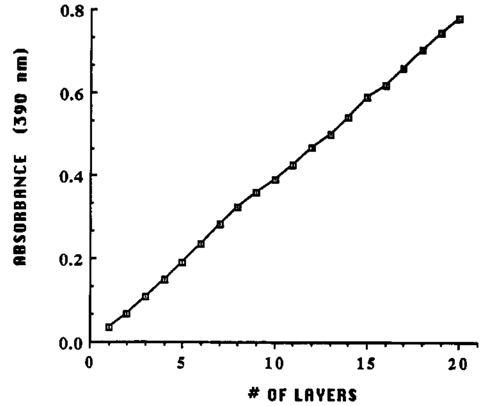


Figure 3. Maximum UV–vis absorbance vs layer number for Zr–QDP on glass, deposited on both sides of a glass slide as described in the Experimental Section.

Preparation and Properties of Multilayers. Multilayer coatings were deposited on Si, glass, and mica-supported gold. Plots of ellipsometric thickness vs layer

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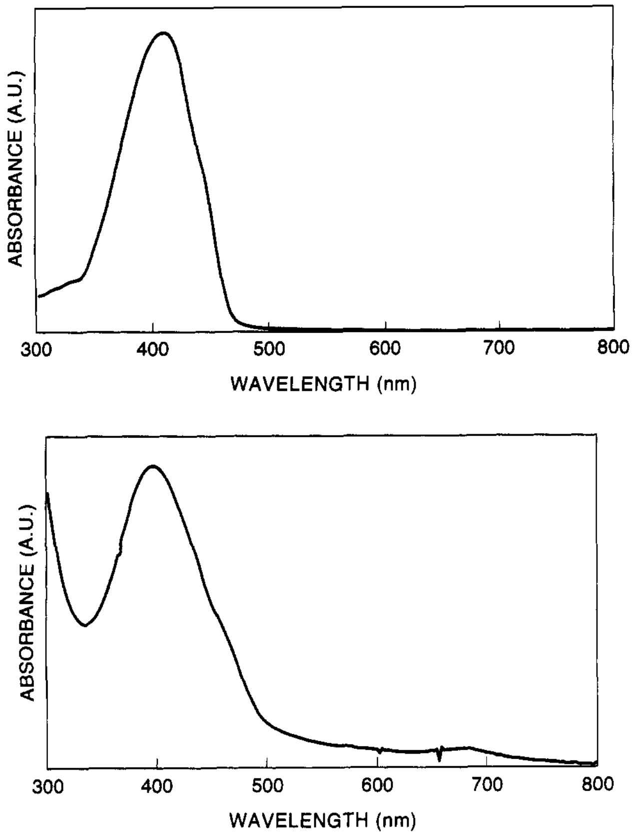

Figure 4. UV-vis spectrum of QDP (top) as a 1.9×10^{-4} M solution in DMSO and (bottom) as a 12-layer film after 5-min exposure to Br_2 vapor.

number for the multilayer on one surface of a Si wafer and of absorbance vs layer number for the multilayer on both sides of a glass slide are shown in Figures 2 and 3, respectively. The ellipsometric thickness increment per layer rose slightly as layers were accumulated on Si, which may reflect slightly incomplete layer formation in the first few deposition cycles. The ellipsometric thickness of 12 layers on gold was 19 Å/layer.

The extinction coefficient of QDP in DMSO at its absorbance maximum, derived from the spectrum given in Figure 4, top, is 3.4×10^4 M^{-1} cm^{-1}. From the absorbances plotted in Figure 3, a thickness per layer of 20 Å was determined for the multilayers by using a QDP concentration of 2.7 M derived from either the molecular volume calculated from molecular models or the crystallographic density[15] of thiophene oligomers. The result is in excellent agreement with the ellipsometric thicknesses and predictions of molecular models.[23]

The Zr content of a 12-layer film on silicon was determined by using X-ray fluorescence (XRF) spectroscopy. The less sensitive Zr Kα emission (15.7 keV) was used because the Lα line (2.0 keV) was obscured by the strong Si emission from the substrate. A calibration curve relating the XRF signal to Zr surface density was determined from films of polymers containing known quantities of $Zr(acac)_4$. A number density of $(3 \pm 1) \times 10^{14}$ Zr atoms/cm^2 was obtained for the 12-layer sample, corresponding to one Zr atom for every 33 ± 11 $Å^2$ of interlayer area. This may be compared to the value of one Zr per 24 $Å^2$/layer that would be projected for crystalline zirconium phosphate, the parent structure, based on a previous determination.[13]

Exposure of QDP-terminated multilayers on glass to Br_2 vapor for several minutes resulted in a weak but definite absorbance at 680 nm, as shown in Figure 4, bottom. This band persisted as long as the sample was in a Br_2-saturated atmosphere but faded in minutes after removal to air. Bromination of well-packed layers did not affect the bulk of the sample, but exposure of intentionally incomplete multilayers resulted in rapid and extensive degradation of the chromophore. Iodine vapor had no effect on the absorbance of QDP films, consistent with the I_2/I^- redox potential ca. 0.9 V more negative than that of the QDP tetraamide. As long as surface adsorption of water or HBr was avoided, the four-point-probe sheet resistance of the films with or without Br_2 treatment was $>10^7$ Ω/square as measured with a 5-10-lb spring-clamp probe and a Keithley digital multimeter. The sheet resistance of an InSnO substrate was 20, 40, 300, and 4×10^8 Ω/square after 0, 1, 2, and 3 layers of QDP were applied, respectively.

Discussion

We have demonstrated the first example of layer-by-layer deposition of a zirconium organodiphosphonate with a nonparaffinic organic core. The conditions developed in this work have been applied to other π-conjugated organophosphonates such as those with azo and phenylene linkages. The apparent pH optimum that we observed may reflect a delicately balanced distribution of deprotonated phosphonate nucleophilic species and protonated zirconium oxide leaving groups that must exist for effective layer formation. The necessity of the 80 °C deposition temperature indicates that steric barriers may be significant in defining the kinetics of layer densification, particularly in layers more than half complete, where the mobility of groups on the surface is more restricted than for sparsely packed layers. These steric effects may be more severe for rigid organics, since assembly of complete layers with polymethylene cores is apparently possible in a few hours at room temperature[12] but, as shown in Table I, is not possible with the quaterthiophene core.

The zirconium number density is a bit less than that expected from the structure of crystalline zirconium phosphate,[13] although the difference is within experimental error. Any lack of registry of the parent zirconium phosphate unit cell with the packing motif of the quaterthiophene would lower the density of the zirconium layer compared to the parent structure. With this in mind, we consider our zirconium analysis, the ellipsometric thickness, and the absorbance data consistent with the formation of the highly ordered, dense film pictured in Figure 1.

Reaction of the QDP film with Br_2, whose standard reduction potential is only 0.3 V below that of the quaterthiophenes, gives a new low-energy absorbance band, as do LB films of thiophene oligomers treated with I_2.[16a-c] The position of the band corresponds roughly to the principal transition for quaterthiophene radical cation.[17c,d] The Br_2-induced band could arise from a simple electron transfer from the film to form radical cations of the QDP and Br^- or could be from a σ-bonded complex. In contrast to the LB film cases, the "doping" process did not seem to extend to the bulk of the film (except for poorly deposited samples), as evidenced by the maintenance of the 380-nm signal, was easily reversed or quenched by removal from the Br_2 atmosphere, and did not lead to markedly higher conductivity. These contrasts may be a consequence of the denser packing of the zirconium films compared to the LB analogues or the presumably more positive oxidation potential of the Zr-QDP film compared to the oxidation potential of larger unsubstituted oligothiophenes

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[23] This analysis also assumes an isotropic transition moment for the multilayer, which the multilayer appears to possess. This assumption will be tested in the future with polarization-dependent spectroscopy.

in LB films. The inability of the four-point probe to penetrate 3 layers of QDP on InSnO is also a tribute to the hardness and coherence of the multilayer. This manifestation of insulating ability parallels the previously reported electrochemical passivation of a gold electrode by an aliphatic zirconium diphosphonate monolayer.[12b]

Future goals of this effort are to exploit both the strength and electronic properties of multilayers prepared by self-assembly. The relative unresponsiveness of such films to chemical, mechanical, and thermal stress point to possible uses in insulation and passivation. We would also like to incorporate this general robustness into films that are more electronically active as a whole. Replacement of the nonoxidizable and nonreducible zirconium phosphonate interlayer with an interlayer that could act as an electron donor or acceptor in its own right is one strategy under consideration for the design of multilayers in which interlayer electron transfer could be observed. The quaterthiophene building block, because of its oxidizability and demonstrated suitability for packing in multilayers, may be appropriate for electroactive multilayered materials.

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Ionic Conductivities of Ion-Exchanged $A_3Sb_3P_2O_{14}$ (A = Na, K, Rb), $A_5Sb_5P_2O_{20}$ (A = Li, Na, K, Rb), and Partially Substituted $K_5Sb_{5-x}M_xP_2O_{20}$ (M = Nb, Ta)

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The ionic conductivities of ion-exchanged compounds were measured in $A_3Sb_3P_2O_{14}$ (A = Na, K, Rb) and $A_5Sb_5P_2O_{20}$ (A = Li, Na, K, Rb) with two-dimensional (2D) layered and three-dimensional (3D) framework structures, respectively. In layered $A_3Sb_3P_2O_{14}$, the mobility of the cations alone determine the ionic conductivity. In $A_5Sb_5P_2O_{20}$ with framework structure, both the bottleneck size and the mobility of the cations affect the observed ionic conductivity. Partial replacement of Sb by Ta/Nb in the highest conducting $K_5Sb_5P_2O_{20}$ sample lead to improvement of the ionic conductivity by 1 order of magnitude ($\sim 10^{-3}$ $(\Omega\ \mathrm{cm})^{-1}$ at 500 °C) in $K_5Sb_3Nb_2P_2O_{20}$. The optimal bottleneck size appears to be in $K_5Sb_3Nb_2P_2O_{20}$, since no further improvement in the ionic conductivity is observed in $K_5Sb_2Ta_3P_2O_{20}$, which has a larger bottleneck than $K_5Sb_3Nb_2P_2O_{20}$.

Introduction

Piffard et al.[1-5] recently reported a series of potassium phosphatoantimonates (K-Sb-P-O), hereafter KPA) with structures ranging from quasi-one-dimensional (1D) to quasi-two-dimensional (2D) to three-dimensional (3D) network. Among these KPAs, the $K_nSb_nP_2O_{3n+5}{\cdot}xH_2O$ (n = 1, 3, 5) series[6-8] has been found to exhibit good ion-exchange properties. During our recent study[9] on the ionic conductivity of these KPAs, we found that the n = 5 member of the series, $K_5Sb_5P_2O_{20}$, has the highest ionic conductivity ($\sim 10^{-3}$ $(\Omega\ \mathrm{cm})^{-1}$ at 500 °C) of all the KPAs investigated. This was attributed to its skeleton structure (Figure 1) with interconnected, large and mostly vacant tunnels that facilitate the motion of K^+ ions. The ionic conductivity of this phase was improved by an order of magnitude when potassium was ion-exchanged by sodium. In this work we investigated the effects of various substitutions on the ionic conductivity of $K_5Sb_5P_2O_{20}$, which includes the isomorphous replacement of Sb^{5+} by V^{5+}, Nb^{5+}, or Ta^{5+} and partial replacement of P^{5+} by Si^{4+}. The former should affect the size of the bottleneck only while the latter will also require an increase in the K^+ content to maintain charge neutrality. Finally, we carried out detailed ion-exchange studies on the 3D $K_5Sb_5P_2O_{20}$ and the layered $K_3Sb_3P_2O_{14}$ in order to compare the ease of ion-exchange with structural dimensionality and the resultant ionic conductivities. These results are presented in this paper.

Experimental Section

$K_3Sb_3P_2O_{14}$ and $K_5Sb_5P_2O_{20}$ were prepared as described previously.[4,5] Partial substitutional reactions were carried out by replacing some of the P_2O_5 by SiO_2 in $K_{5+x}Sb_5P_{2-x}Si_xO_{20}$ and some of the Sb_2O_3 by $V_2O_5/Nb_2O_5/Ta_2O_5$ (all chemicals were at least reagent grade purity) in $K_5Sb_{5-x}M_xP_2O_{20}$ (M = V, Nb, Ta). The reaction temperature varied according to the nature of the substituent: 1000 °C for $K_5Sb_{5-x}V_xP_2O_{20}$, 1070 °C for $K_5Sb_{5-x}Nb_xP_2O_{20}$, and 1100 °C for $K_5Sb_{5-x}Ta_xP_2O_{20}$. Higher reaction temperatures led to melting in the case of vanadium- and niobium-substituted KPAs.

Ion-exchange reactions were carried out via hydrothermal autoclave synthesis, by the molten salt method, or indirectly by the ion-exchange of the protonated phosphatoantimonates.

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