



# The Effects of Pyrrole: Oxidant Ratios on the Permittivity of Conducting Polymer Composites

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**Defence R&D Canada – Atlantic**

Technical Memorandum

DRDC Atlantic TM 2006-208

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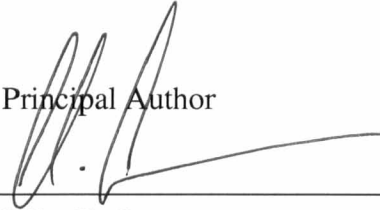
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Principal Author



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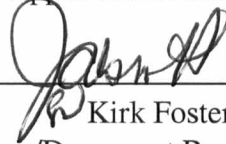
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## Abstract

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Freund's method for cascade polymerization is proving to be a versatile method to produce conducting polymers in a processible manner. One promising avenue for this technology is the creation of composite materials which consist of a interpenetrating network of conducting polymer inside an inert host matrix. Our early work with these composites is showing that they can offer a number of unusual properties.

This paper focuses on clarifying the nature of the oxidant used to date, phosphomolybdic acid (PMA), and its role in the process. Polypyrrole–polyurethane composites of varying loading levels were made and their permittivity measured, with percolation occurring near 4% v/v. The ratio of pyrrole monomer to oxidant was varied over a range from 12:1 to 1:2. Insufficient oxidant led to incomplete polymerization and hence poor permittivity. Excess oxidant left trapped ions in the composites which led to secondary dielectric effects. A ratio of around 2.5:1 appears to be a reasonable compromise.

The cyclic voltammetry of PMA in tetrahydrofuran reveals a pair of quasi-reversible waves near 0.4 V and 0.6 V *vs.* SCE. The position of these waves is pH-dependent.

## Résumé

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La méthode de polymérisation à croissance contrôlée conçue par M.S.Freund se démontre comme un façon polyvalent pour produire des polymères conducteurs dans une manière transformable. Une application prometteuse de cette technologie est la création des matériaux composites qui consistent des réseaux interpénétrants de polymère conducteur à l'intérieur d'un hôte en polymère inerte. Nos travaux préliminaires avec ces matériaux composites démontrent plusieurs propriétés remarquables.

Ce rapport vise à clarifier la nature de l'oxydant, acide phosphomolybique (PMA), et son rôle dans le processus. De divers matériaux composites polypyrrole-polyuréthane ont été préparés et on a mesuré leur permittivité, trouvant la percolation à environ 4% v/v. On a varié le ratio de monomère pyrrole à l'oxydant sur une gamme de 12 :1 à 1 :2. Une quantité insuffisante de l'oxydant a mené à une polymérisation incomplète, et alors, une permittivité basse. Un excès d'oxydant laisse des ions occlus produisant des effets diélectriques secondaires. Un ratio d'environ 2,5 :1 se montre comme un compromis satisfaisant.

La voltampérométrie cyclique du PMA en tetrahydrofuran révèle deux ondes quasi-reversibles proche de 0,4 V et 0,6 V *vs.* SCE. La position de ces ondes est dépendant du pH.

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## Executive summary

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### The Effects of Pyrrole:Oxidant Ratios on the Permittivity of Conducting Polymer Composites

Colin G. Cameron, Peter J. O'Hagan; Defence R&D Canada – Atlantic TM 2006-208;  
Defence R&D Canada – Atlantic; November 2006.

**Background:** Since their discovery in the 1970s, conducting polymers have offered the promise of numerous interesting applications. Military technologies that could benefit include electrochromics, energy storage, radio frequency radiation shielding, and anti-corrosive coatings. However, some thirty years later, very few of these polymers have become anything more than a laboratory curiosity. The primary reason for this stall in development is that the poor processibility of most conducting polymers means that they cannot be formed into useful physical structures.

A recent breakthrough is the new polymerization technique developed by M.S. Freund. This method permits the slow and controlled growth of the polymer in such a way that it can be, for example, painted or spin coated on an arbitrary surface, and even grown inside another polymer. This last point is especially noteworthy, since this arrangement produces hybrid materials that combine the desirable electronic properties of a conducting polymer with the robust mechanical properties of an inert support host. However, the polymerization mechanism is not fully understood at this time.

**Principal Findings:** This study makes some progress towards understanding the polymerization mechanism by examining the oxidant (phosphomolybdic acid) used in the reaction. Composites of polypyrrole and Pellethane (a commercial thermoplastic polyurethane elastomer) were formed with a range of conducting polymer loadings and also different ratios of oxidant. The dielectric properties of these composites were compared to understand the effects of loading and oxidant ratio, as well as the related problems of trapped ions.

The electrochemical properties of phosphomolybdic acid alone were studied in tetrahydrofuran, the solvent used in the experimental procedure. The properties of this oxidant are known to vary greatly depending on its environment, and its redox potential in tetrahydrofuran is not known in the literature.

**Significance of Findings:** Freund's polymerization method has been previously shown to be a versatile and promising technique for synthesizing conducting polymers and their composites. This is an important step towards creating useful technologies based on these materials. A clear understanding of the chemical process will enable its refinement, and

the present work helps to elucidate a key component of the reaction, the oxidant. Optimizing the balance of polymer loading and oxidant ratio is considered, and the pitfalls of phosphomolybdic acid are underlined.

**Future Work:** Future work will continue to refine this important method of creating conducting polymer composites. Since phosphomolybdic acid has a number of undesirable traits, we intend to explore other oxidants using the same pyrrole–Pellethane system. Finally, other conducting polymers and support matrices will be considered in order to target specific properties.



# Sommaire

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## The Effects of Pyrrole:Oxidant Ratios on the Permittivity of Conducting Polymer Composites

Colin G. Cameron, Peter J. O'Hagan; Defence R&D Canada – Atlantic TM 2006-208;  
R & D pour la défense Canada – Atlantique; novembre 2006.

**Contexte:** Depuis leur découverte aux années 1970, les polymères conducteurs promettaient de nombreuses applications intéressantes. Les technologies militaires qui pourraient en profiter incluent les matériaux électrochromiques, le stockage de l'énergie, le blindage contre les radiofréquences, et l'inhibition de corrosion. Toutefois, après une trentaine d'années, peu de ces polymères se sont trouvés au-delà du niveau de laboratoire. La raison primordiale de ce calage de développement est la mauvaise transformabilité de la majorité de ces polymères, signifiant une incapacité d'être façonnés en formes utiles.

Un important progrès technologique est la nouvelle méthode de polymérisation conçue par M.S. Freund. Cette façon d'aborder la problème de la mauvaise transformabilité en laissant croître le polymère dans une façon lente et contrôlée. Donc il est possible d'appliquer le polymère conducteur par peindre, par le dépôt à la tournette, ou même le créer dans un autre polymère hôte. Ceci est surtout important, car un tel matériau composite hybride aura les propriétés électroniques désirables du polymère conducteur ainsi que les propriétés mécaniques d'un support robuste. Toutefois, le mécanisme chimique du polymérisation n'est pas clair.

**Résultats:** La présente étude fait des progrès à comprendre le mécanisme chimique du polymérisation par examiner l'oxydant (l'acide phosphomolybique) exigé par la réaction. On a formé des matériaux composites de polypyrrole avec Pellethane (un élastomère thermoplastique en polyuréthane) dans une gamme de chargement de polymère conducteur et aussi utilisant de divers fractions d'oxydant. On a comparé les propriétés diélectriques afin d'étudier les effets de chargement, du ratio, et la problème d'ions occlusés.

Les propriétés électrochromiques de l'acide phosphomolybique ont été examinées dans le solvant du processus, tétrahydrofuran. On connaît que les caractéristiques de cet oxydant sont variables, et le potentiel électrochromique en tétrahydrofuran est cependant inconnu dans la littérature.

**Portée:** La méthode de Freund a été auparavant démontrée d'être une technique polyvalente et prometteuse pour synthétiser les polymères conducteurs et leurs composites. Ceci représente une importante étape envers développer des technologies basées sur ces matériaux. Une compréhension claire du processus mènera à son raffinement, et la présente

œuvre élucide partiellement la nature d'une partie importante de la réaction, l'oxydant. On considère l'optimisation de l'équilibre de chargement de polymère et le ratio d'oxydant. Les problèmes associés avec l'acide phosphomolybique sont soulignés.

**Recherches futures:** Les recherches futures viseront à perfectionner cette méthode importante pour créer les matériaux composites de polymère conducteur. On a trouvé que l'acide phosphomolybique a de nombreux traits indésirables, alors on explorera d'autres oxydants dans le cadre du système pyrrole-Pellethane. Finalement, on considèrera d'autres combinaisons de polymères conducteurs et hôtes afin d'obtenir des caractéristiques spécifiques.

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# 1 Background

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Defence R&D Canada has had a long-standing interest in dielectric materials and composites for advanced military applications. Such technologies include actuators, sensors, electromagnetic shielding, corrosion inhibition, energy storage, and adaptive camouflage. This is illustrated in part by the support of Technology Investment Fund (TIF) programs in areas such as supercapacitors and Maxwell Stress Actuators. For the latter, the response is linearly proportional to the permittivity of the material used in the elastomer core. Consequently, there was motivation to make new elastomeric materials with elevated dielectric constants.

Early materials were based on elastomers filled with non-conductive, high-dielectric ceramics [1,2] such as barium titanate, lead magnesium niobate-lead titanate, and poly(copper phthalocyanine). The basis for this approach was that there should be an increase of the dielectric constant of a composite ( $\epsilon_c$ ) consisting of a low-permittivity host matrix ( $\epsilon_m$ ) filled with a high-permittivity guest ( $\epsilon_f$ ;  $\epsilon_f \gg \epsilon_m$ ), and that this increase should follow the volume fraction ( $\phi_v$ ) relationship proposed by Bruggemann [3]:

$$\frac{\epsilon_c}{\epsilon_m} = \frac{1}{(1 - \phi_v)^3} \quad (1)$$

Results were consistent with equation 1, but the magnitude of increased permittivity was not satisfactory. Attention was then turned to elastomers with conductive fillers such as graphite [4, 5] and discrete polypyrrole particles [6]. The premise for using conductive fillers is that near the percolation threshold<sup>1</sup> the dielectric properties of such a system increase rapidly, following a power law relationship [7, 8]. The McLachlan effective medium equation (Eq. 2) describes this phenomenon, relating the conductivity of the system ( $\sigma$ ) to that of the filler ( $\sigma_f$ , relatively high) and the matrix ( $\sigma_m$ , relatively low) via a fitting parameter  $t$ . At the percolation threshold  $\phi_C$ , the conductivity undergoes a rapid sigmoidal change. A similar expression can be derived for permittivity  $\epsilon$ .

$$\frac{\phi(\sigma_f^{1/t} - \sigma^{1/t})}{\sigma_f^{1/t} + [(1 - \phi_C)/\phi_C]\sigma^{1/t}} + \frac{(1 - \phi)(\sigma_m^{1/t} - \sigma^{1/t})}{\sigma_m^{1/t} + [(1 - \phi_C)/\phi_C]\sigma^{1/t}} = 0 \quad (2)$$

---

<sup>1</sup>The percolation threshold is a critical concentration of conducting filler at which electrons are able to find a pathway from one side of the sample to the other. They do so by hopping or “percolating” from particle to particle under the influence of an applied electric field. The phenomenon has a lesser dependency on the magnitude of the electric field in addition to its frequency.

More simply expressed, at loadings  $\varphi > \varphi_C$ , the conductivity  $\sigma$  follows this relationship:

$$\sigma \propto (\varphi - \varphi_C)^{t_1} \quad (3)$$

At loadings  $\varphi < \varphi_C$ , the permittivity is given by:

$$\varepsilon \propto (\varphi_C - \varphi)^{-t_2} \quad (4)$$

The exponents  $t_1$  and  $t_2$  are fit parameters.

Equations 1 and 4 imply that conductive fillers will lead to higher permittivities than can be reached with non-conductive fillers at the same loading level. We found this to be true with graphite-filled polyurethane systems, where  $\varepsilon$  increased by a factor of nearly 600 was observed at a loading level of 18% v/v [4, 5], compared to a mere tenfold increase in  $\varepsilon$  at 40% v/v for non-conductive titanium dioxide in silicone [1]. This is an important point, since these fillers tend to have pronounced influences on the mechanical properties of the composite.

In order to reduce the loading levels further, dielectric composites based on conductive particles with a high aspect ratio such as carbon nanotubes [9] were developed. As the group's research turned to dielectrics for energy storage, these filled composites remained of interest. Polyurethane/polypyrrole composites have been one area of particular interest since it became apparent that Freund's method of controlled growth polymerization [10, 11] could be used to grow interpenetrating conducting polymer networks. Such networks could provide the desired enhanced dielectric properties of a near-percolative system but with loading levels significantly lower than for other fillers such as graphite.

An important consideration of percolative dielectrics is the concomitant increase in dielectric loss, *i.e.*, conductivity. This could be a concern when attempting to use such materials in traditional capacitors without added precautions (such as including insulating layers), and our group will be exploring this issue in the future. Nonetheless, lossy percolative dielectrics are potentially very useful in a number of other areas, including electromagnetic shielding and electrochromics. This is especially true of composite materials based on conducting polymers in an inert host, owing to the inherent robustness of these composites.

The current report documents progress made toward developing a better understanding of the process used to create conducting polymer composites. It focuses on the oxidant (phosphomolybdic acid) used to drive Freund's polymerization reaction.

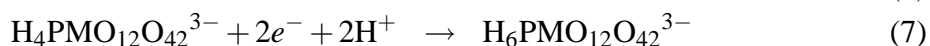
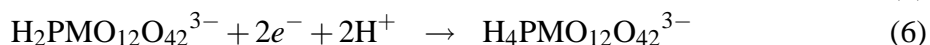
## 1.1 Phosphomolybdic acid electrochemistry

Phosphomolybdic acid is one of a number of Keggin-type polyoxometallates having the general form  $\text{XM}_{12}\text{O}_{40}^{n-}$ . Such materials have been of interest lately for their useful properties, particularly as highly selective electrocatalysts. Their electrochemistry typically



exhibits several one- and two- electron reversible redox transitions that produce intensely blue coloured mixed-valence products. Additional irreversible electron transfers are also available.

The  $\alpha$ -Keggin heteropolyanion phosphopolyoxomolybdenate (or phosphomolybdenate) exhibits rich but easily varied electrochemistry [12]. It is also fairly easily hydrolyzed, complicating its behaviour further in aqueous environments. Five two-electron reductions can be observed in mixed organic-aqueous systems containing acid. In the presence of cyclic ethers such as THF or 1,4-dioxane, further irreversible two-electron transfers are observed. The reduction potentials are pH dependent due to protonation:



In organic media, the electrochemistry is highly solvent dependent owing to stabilization of the reduction products by the solvent. For example, three reversible one-electron waves are observed in acetonitrile, at  $E_{1/2} = -0.170, -0.585, \text{ and } -1.313 \text{ V vs. Ag/Ag}^{+}$ . These convert to two-electron waves when acid is added.

## 2 Experimental Procedure

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### 2.1 Approach

One purpose of these experiments was to determine what effect, if any, varying the ratio of pyrrole:oxidant had on the conductive polymer composite. The method described previously [10, 11, 13] used a 2:1 ratio of pyrrole:oxidant. In the present set of experiments, pyrrole:oxidant was varied over a range of 12:1 to 1:2. The permittivity of the resulting composites was measured in order to ascertain the overall percolative quality of the system; a high permittivity implies good long-range charge mobility. The weight fraction of pyrrole in the composite was also varied.

### 2.2 Materials

#### 2.2.1 General

Pellethane 2103-70A is a commercial thermoplastic polyurethane with Shore A hardness of 70. It was received from Dow Corning as small pellets and used with no further purification. Tetrahydrofuran (THF, Fisher 1B grade) was used as received and stored over molecular sieves. Pyrrole (98%, Aldrich) was purified by passing the liquid through a short column of basic alumina until the eluent was nearly colourless.

Samples were mixed and cast in disposable aluminum weighing dishes: Fisher Scientific smooth-walled type, 65 mm diameter, stock number 08-732-103.

## 2.2.2 Phosphomolybdic acid hydrate

Phosphomolybdic acid hydrate (PMA, formula  $H_3[P(Mo_3O_{10})_4] \cdot xH_2O$ ) from both Fisher and Sigma-Aldrich was used as received. To determine the molybdenum content of the PMA from the two different companies, samples were analyzed using an Agilent 7500-series Inductively Coupled Plasma Mass Spectrometer (ICP-MS). It was determined that the PMA obtained from Sigma-Aldrich contained 44.5% w/w Mo while the Fisher reagent had a Mo content of 49% w/w. The difference between the two was probably due to a greater degree of crystal hydration in the Sigma-Aldrich formulation, which gave a corresponding formula weight of around 2550 g/mol. The calculated formula weight for the Fisher product was 2366 g/mol. However both were found to have a P:Mo ratio of 1:12, confirming that they were the essentially the same chemical, other than for water content.

In the current work, PMA content was calculated using the molecular weights estimated from the ICP-MS experiments.

## 2.3 Sample Preparation

The Pellethane was weighed using an analytical balance, then dissolved in tetrahydrofuran (THF) in a glass beaker. Because the Pellethane needed to swell before dissolving, this process generally took between 8 and 12 hours. Pyrrole was filtered through a short alumina column to remove oligomers and any other impurities, then weighed out in an aluminum weigh dish to obtain the desired loading level. The pyrrole was added to the dissolved Pellethane solution in the beaker, and additional THF was used to wash down the weigh boat to ensure all the pyrrole was transferred.

Phosphomolybdic acid was then weighed into an aluminum weigh boat, dissolved in THF and added to the solution of Pellethane and pyrrole. The combined solution was stirred with a glass rod to ensure it was well mixed. The solution was then poured off into one weigh boat, or evenly into two if the volume of the solution required. To slow the drying process by creating a THF-rich atmosphere, each sample was placed underneath a 600 mL beaker until dried, which generally took 24 hours, although with higher amounts of PMA, the samples took up to 36 hours to dry. The dry samples were then removed from their moulds and each placed in a pouch fashioned from two 110 mm diameter filter papers. They were placed in a Soxhlet apparatus and extracted with methanol overnight until the blue colour of reduced PMA products was no longer visible in the extract.

In order to follow the form of the model equations and to be consistent with our previous work, the weight fraction of filler ( $\phi_w$ ) was converted to volume fraction ( $\phi_v$ ) according to Equation 8:

$$\phi_v = \frac{m_f \rho_m}{m_f \rho_m + m_m \rho_f} \quad (8)$$

where  $m_m$  and  $m_f$  are the masses of matrix and filler, respectively, and  $\rho_m$  and  $\rho_f$  are their densities. For Pellethane,  $\rho_m = 1.06 \text{ g/cm}^3$ , and for polypyrrole,  $\rho_f = 1.3 \text{ g/cm}^3$ . For this system, 2% by weight is approximately 1.6% by volume.

## 2.4 Measurement of permittivity

The permittivity was measured at constant temperature (20°C) over a frequency range of 0.01 Hz to 100 kHz using a ceramic parallel plate dielectric analysis (DEA) apparatus (TA Instruments model 2970). The permittivity at 1 Hz was arbitrarily chosen as a point of comparison between all the samples.

## 2.5 Cyclic voltammetry

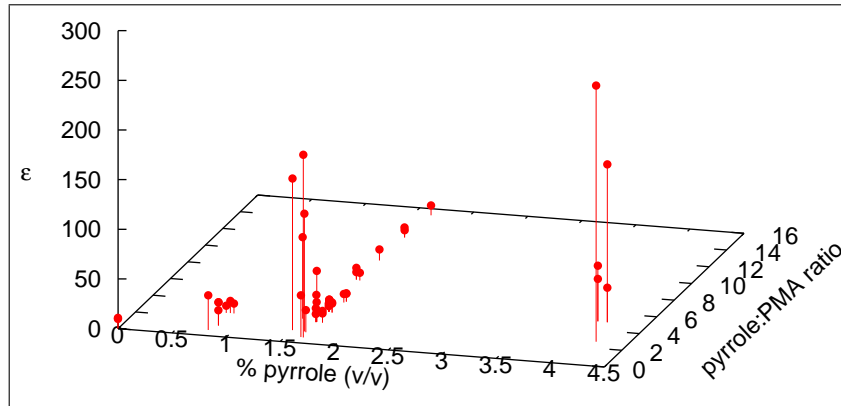
The electrochemistry of PMA was recorded as a 1.0 mM solution in THF containing 0.10 M LiClO<sub>4</sub>. A three-electrode configuration was employed, using a platinum disc working electrode ( $A = 0.0075 \text{ cm}^2$ ), a saturated calomel reference electrode (SCE), and a platinum wire counter electrode. Cyclic voltammograms were acquired with an EG&G PAR 273 potentiostat and recorded on a Linux computer system equipped with a National Instruments PCI-6036E data acquisition card using custom software and the *libcomedi* interface library.

# 3 Results

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## 3.1 Sample preparation problems

Several different methods for preparing the samples were attempted. One method employed a stock solution of dissolved Pellethane in THF in a stoppered Erlenmeyer flask. The concentration of the solutions used varied between 10 and 20% w/w. The absolute concentration of the stock solutions was determined by weighing a small portion of the solution, and weighing it again after all the solvent had evaporated. The main advantage of this approach was that it was not necessary to make small separate amounts of dissolved Pellethane for each sample, leading to a significant savings in time. However, it was difficult to make samples of a consistent size and composition owing to the necessity for rapid pouring. Further problems were encountered in weighing the samples due to the rapid evaporation of the solvent THF.



**Figure 1:** Results from the DEA analysis. The permittivity  $\epsilon$  shown was measured at 1 Hz

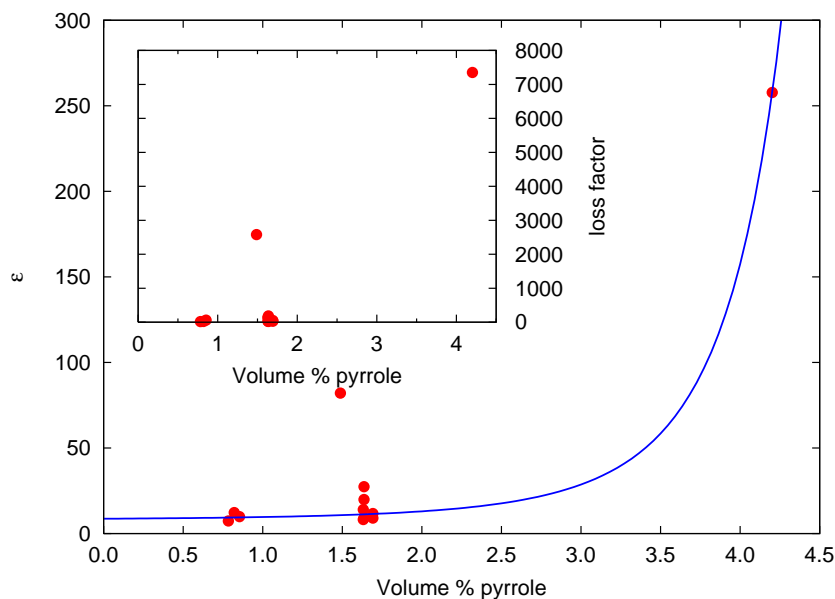
It was also found that samples thinner than around 0.2 mm were prone to wrinkling, and that the ideal thickness for the films was between 0.4 mm and 0.6 mm. Using the Fisher weigh boats as molds, it was found that using approximately 1.5 g of Pellethane produced a film approximately 0.5 mm thick. Also, if using an amount of oxidant higher than the 2:1 pyrrole:PMA ratio, the excess PMA tended to settle out on the bottom of the pan which led to an uneven surface after drying. Wrinkling, PMA-induced roughness, and visible inhomogeneities resulted in many samples being discarded since the properties of such samples cannot be reliably characterized with the DEA instrument. Consequently, the current experimental procedure is in need of refinement. A more precise protocol could be put in place once the relationships between experimental parameters are better understood.

## 3.2 Permittivity

Permittivity was measured for a series of samples having various loading levels of pyrrole and ratios of oxidant to pyrrole. A complete overview of the data is presented in Figure 1. Data presented in subsequent Figures 2 and 3 are two dimensional slices of this set.

### 3.2.1 The effects of varying loading level on permittivity

As expected from the percolation model, the permittivity increased as the loading level of pyrrole in the samples increased. The loading level was however deliberately kept below the percolation threshold in these experiments. Doing so allowed the reliable use of the dielectric analyzer; this instrument has difficulty measuring the permittivity of very lossy (*i.e.*, slightly conductive) materials. The companion study by Mossman and Cameron [14] examines in closer detail the properties of these systems near and beyond the percolation threshold.

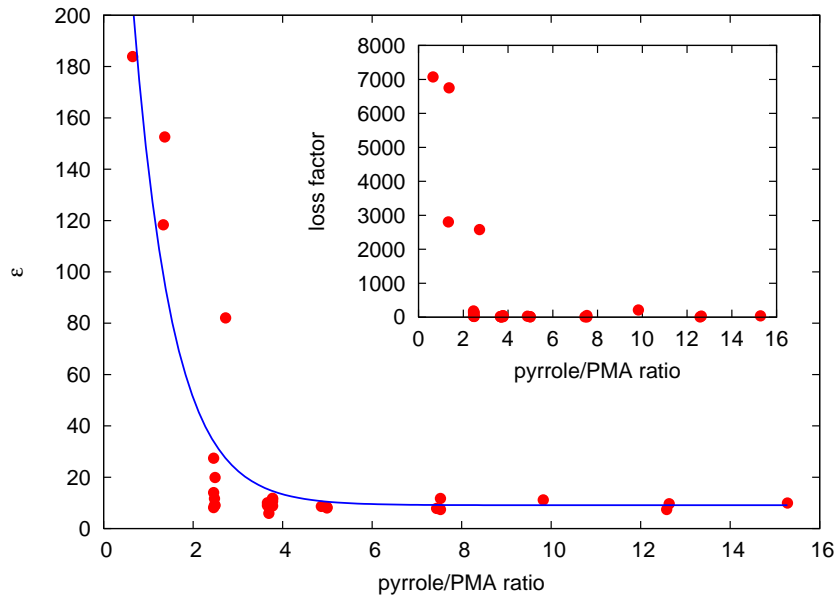


**Figure 2:** Increase in permittivity at higher loading levels for composites generated using a constant oxidant ratio, approximately 2.5:1. Measurements were taken at 1 Hz and at 20°C. The fit line is of the form given by Equation 4. Inset: Loss factor as a function of loading level.

Figure 2 illustrates the rise in permittivity for increased polymer loading levels using a constant  $\approx 2.5:1$  pyrrole:PMA ratio. The trend follows a relationship consistent with the percolation model. Two points are noteworthy. First, the percolation threshold in this system appears to be in the vicinity of 4% v/v (which corresponds to 5% w/w). This is somewhat higher than that found in other experiments [14]. Second, an outlying point appears near 2% loading level. Both these observations suggest that the overall properties of the system can be very sensitive to the experimental conditions. This can be problematic since not all these conditions are understood at this point. In the present case however, there were sufficient repetitions in the more important regions of the set. This suggests the relative changes in properties are suitable for comparison, and hence the conclusions reached herein are valid.

### 3.2.2 The effects of oxidant ratio on permittivity

Despite the repeated successful application of Freund's cascade growth polymerization, the electrochemical stoichiometry of PMA is still unclear: Does PMA ( $H_3[P(Mo_3O_{10})_4]$ ) transfer one, two, three, four, or six electrons per molecule? Or perhaps some other number? Freund's procedure [10, 11, 13] calls for a 2:1 pyrrole:PMA ratio, yet it is not clear why. The mechanism behind pyrrole polymerization demands that two electrons must be transferred for every molecule of pyrrole added to the chain. Using the 2:1 ratio, this



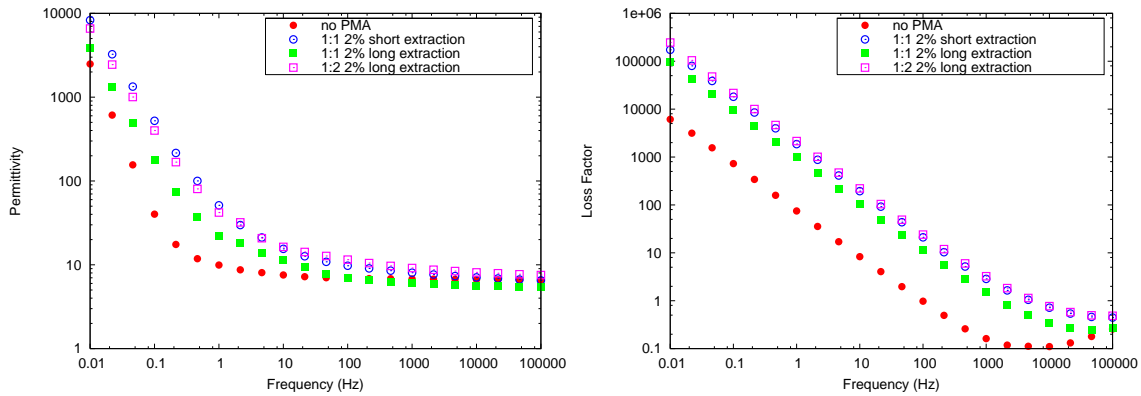
**Figure 3:** Permittivities of composites having 2% (w/w) pyrrole loading level and varying pyrrole:PMA ratios. Inset: Dielectric loss factors of the composites.

implies that four electrons are transferred per molecule of PMA if the resulting polymerization is 100% complete and the product is not in its oxidized form (which is unlikely due to its having a lower oxidation potential than the pyrrole monomer alone). If more than four electrons are transferred per molecule of PMA, then this would provide the slight stoichiometric excess needed to ensure complete polymerization as well as to oxidize the polymer to make it conductive.

A study was undertaken to examine the effects of deviating from the 2:1 ratio using loading levels below the percolation threshold. This differs from Freund's early exploration of this concept [11] which examined DC conductivity alone.

Experimentally, it was demonstrated that as the relative amount of PMA increases, the permittivity of the sample also increases. The greatest permittivity increase came in the range of 2:1 through to 1:2 for pyrrole:PMA. This trend is evident in Figure 3. At lower oxidant levels, the permittivity drops, and by around 5:1 pyrrole:PMA, the permittivity of the composite is essentially unchanged from that of pure Pellethane. This implies that incomplete polymerization had taken place in the samples in which less PMA was used, and the approximately 4:1 range resulted in only partial polymerization and/or incompletely oxidized (*i.e.*, non-conductive) polymer.

The samples with greater PMA loadings had higher permittivity still, although there could be other factors at play, such as the effects of residual PMA ions.



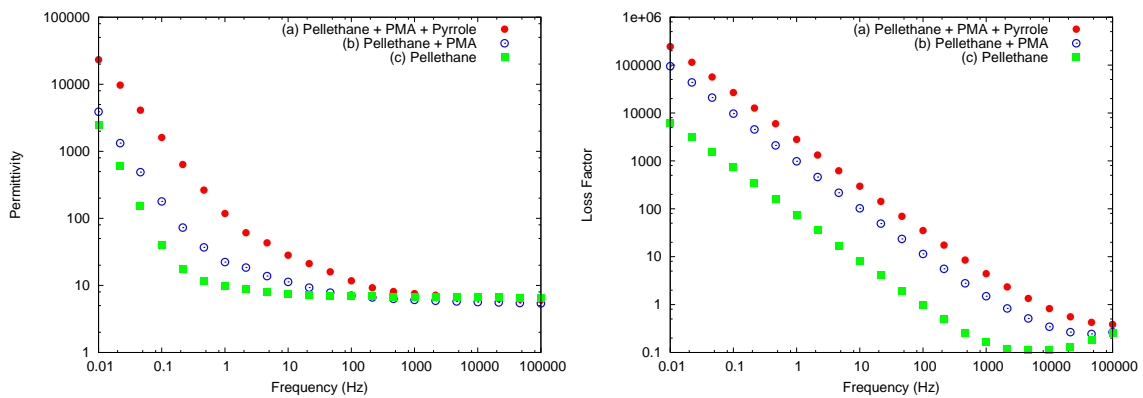
**Figure 4:** DEA spectra showing permittivity and dielectric loss trends in “blank” Pellethane samples containing PMA.

### 3.2.3 The influence of residual PMA

Blank samples were prepared using the same procedure as for the 2% loaded films, but leaving out the pyrrole. Despite careful extraction, it was impossible to remove all the molybdenate ions from the films as indicated by a persistent blue coloration. It was clear from a visual inspection of these samples that there were regions with concentrated amounts of PMA, predominantly in folds and wrinkles, indicating that the extraction process does not uniformly remove the PMA and its products from the composites.

These samples with simulated pyrrole loading demonstrated permittivity higher than that of pure Pellethane. The degree of this enhancement correlates with the total quantity of PMA and duration of the extraction process. This is illustrated in the permittivities and loss factors shown in Figure 4. Similar samples extracted for a shorter period of time exhibited a somewhat higher permittivity, as did samples containing more initial PMA. Since both conditions would presumably lead to a greater quantity of residual PMA, it is fair to speculate that trapped molybdenate ions can lead to enhanced permittivity. This is especially true at low frequencies, consistent with the relatively low mobility of these ionic charge carriers.

Trapped ions are a concern, since the presence of spurious ions even in these blank samples leads to unexpected changes in the properties of the composites. This effect is illustrated in Figure 5. Films having residual molybdenate ions that escaped the rinsing process have permittivity significantly higher than those made from Pellethane alone. Fortunately, the dominant increase in permittivity arises from the polypyrrole. However, the presence of residual ions is problematic as this can lead to poor reproducibility. This issue may be alleviated by choosing an oxidant that can be more easily removed from the matrix.



**Figure 5:** Permittivity and loss factor illustrating the contribution of molybdenate ions in samples with: (a) 2% loading with 1:1 oxidant ratio, (b) same, but without pyrrole, and (c) pure Pellethane subjected to the casting process.



**Table 1:** Cyclic voltammetry data for PMA in THF. Peak potentials are in volts vs. SCE, and peak separations are given in mV.

v (mV/s)	H <sup>+</sup> ?	Wave 1				Wave 2			
		$E_{pa}$	$E_{pc}$	$\Delta E_p$	$E_{1/2}$	$E_{pa}$	$E_{pc}$	$\Delta E_p$	$E_{1/2}$
10	no	0.481	0.349	132	0.415	0.668	0.535	133	0.602
100	no	0.450	0.261	189	0.356	0.647	0.452	195	0.550
100	yes	0.509	0.308	201	0.409	0.704	0.492	212	0.598

### 3.3 Electrochemistry of PMA in THF

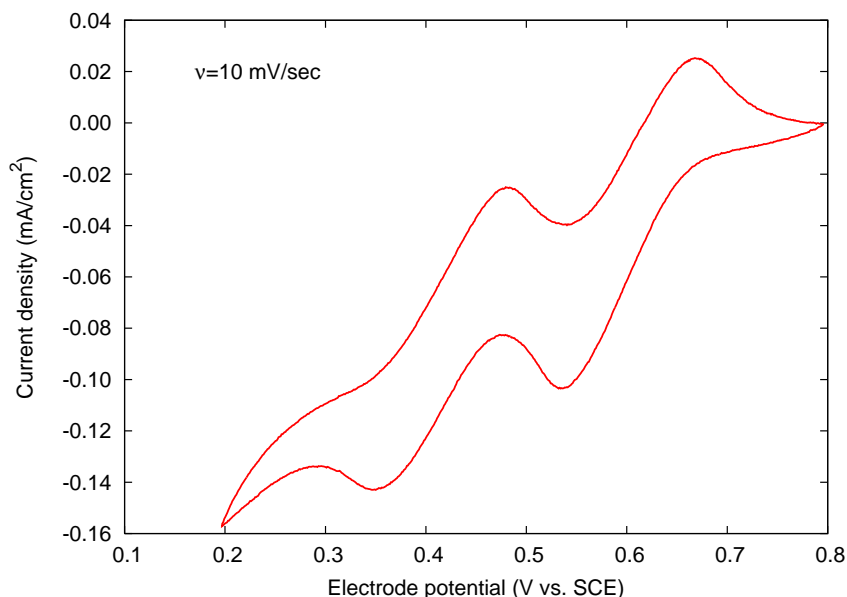
The cyclic voltammetry of PMA in THF exhibits two quasi-reversible waves at moderately positive potentials (near 0.4 and 0.6 V vs. SCE), as illustrated in Figure 6 and summarized in Table 1. The positions of these waves are at potentials significantly more positive than those measured in acetone and acetonitrile [15]. In acetone,  $E_{1/2}(1)$  and  $E_{1/2}(2)$  occur at  $-0.661$  and  $-1.095$  V vs. Ag/Ag<sup>+</sup>, respectively. In acetonitrile, these waves are at  $-0.170$  and  $-0.585$  V vs. Ag/Ag<sup>+</sup>.<sup>2</sup> Clearly the stabilization of redox products by the solvent has an enormous influence on the formal potential of the couples. Unlike the situation in the other two solvents, the redox waves in THF are quasi-reversible: the peak separation  $\Delta E_p = E_{pa} - E_{pc}$  is significantly larger than the 56.5 mV separation expected for a system with rapid electron transfer kinetics, and  $\Delta E_p$  increases with faster sweep rates.

The redox potentials also have a dependence on pH. The addition of one drop of concentrated perchloric acid to the solution leads to an approximately 50 mV shift to more positive potentials, shown in Figure 7. This is consistent with a proton-coupled electron transfer mechanism such as the ones described by equations 5–7.

<sup>2</sup>In the original paper,  $E_{1/2}$  values are measured against a Ag/Ag<sup>+</sup> reference electrode, containing 0.01 M Ag<sup>+</sup> in either acetonitrile or acetone. This couple is frequently used in non-aqueous systems in order to avoid the small (and unpredictable) errors that arise from the junction potential that exists between the reference electrode solution and the experiment solution. The formal potential of this Ag/Ag<sup>+</sup> couple changes depending on the filling solution. Furthermore, the overall reference potential is not necessarily the same under different experimental conditions; Ag/Ag<sup>+</sup> is a *pseudoreference* electrode.

Normally this problem is addressed by measuring the half-wave potential of the ferrocenium/ferrocene couple with this reference electrode under conditions identical to those of one's experiment. If appropriate, ferrocene can be simply added to the experiment as an internal standard. The ferrocenium/ferrocene couple is a good choice as a standard since it is thought to have the same redox potential in all solvents [16].

The authors of the cited reference [15] failed to include such a standard, and so their careful measurements are not absolutely meaningful. An unrelated study [17] reports the ferrocene couple in acetonitrile at  $+0.089$  V vs. Ag/Ag<sup>+</sup> (0.01 M in acetonitrile). Since the same couple occurs at 0.31 V vs. SCE [18], one can attempt to convert the literature PMA half-wave potentials in acetonitrile to the SCE scale:  $E_{1/2}(1)$  and  $E_{1/2}(2)$  occur at  $-0.44$  and  $-1.87$  V. A similar comparison for acetone cannot be made accurately since there is no data for the ferrocene couple against an acetone-filled reference. If one makes the (very poor) assumption that it is the same as the acetonitrile case, this would give  $E_{1/2}(1) = 0.05$  and  $E_{1/2}(2) = -0.36$  V vs. SCE.



**Figure 6:** Cyclic voltammetry of 1 mM PMA in THF containing 0.10 M LiClO<sub>4</sub> at a platinum disc electrode,  $A = 0.0075 \text{ cm}^2$ .

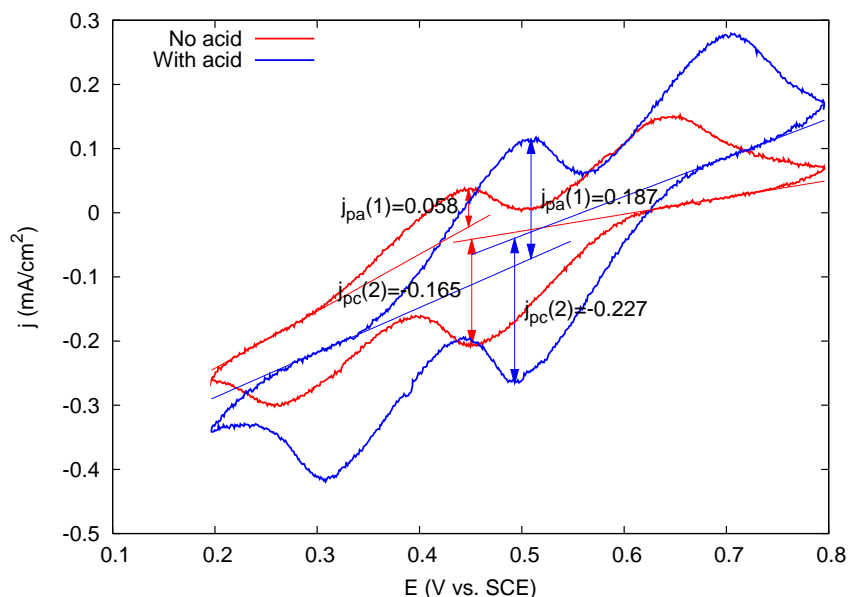
Unlike the cases in acetonitrile or acetone, the addition of acid to the THF system has no clear effect on the number of electrons transferred per wave. Peak current estimates are presented in Figure 7 for the anodic part of wave 1 and for the cathodic part of wave 2. Due to the quasi-reversibility of the waves it is difficult to make conclusions about the total number of electrons transferred on the basis of current alone. However these peak currents can be useful as a relative comparison.

In Figure 7, peak current densities  $j_{pc}(2)$  for the non-acidified sample, and  $j_{pa}(1)$  and  $j_{pc}(2)$  for the acidified sample are of comparable magnitude ( $j_{pa}(1)$  for the non-acidified sample is probably erroneous due to difficulty in establishing an accurate baseline for this wave). This indicates that (i) these waves all involve the same number of electrons transferred, and (ii) acidification does not change the number of electrons involved in the process.

## 4 Conclusions

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These experiments have shown that the approximate 2.5:1 ratio of pyrrole:PMA works reasonably well. Samples prepared with less oxidant showed no enhancement of permittivity. Samples prepared with more oxidant showed increased permittivity, although there is the added issue of trapped ions. If PMA transfers four electrons, then this 2.5:1 ratio may in fact be stoichiometrically deficient: each pyrrole monomer requires two electrons for complete polymerization to the neutral state, which implies a 2:1 ratio. An excess of oxidant is



**Figure 7:** Cyclic voltammetry ( $v = 100 \text{ mV/s}$ ) of PMA before and after the addition of a drop of perchloric acid.

required to generate charge carriers to make the polymer conductive. To reach maximum conductivity (50% oxidation) in a fully-formed polymer, 2.5 electrons per monomer would be needed. This corresponds to a pyrrole:PMA ratio of 3:2 if PMA transfers four electrons. Follow-up studies should attempt (i) to ascertain the maximum yield of polymerization under typical circumstances, and (ii) closer study of PMA electrochemistry to clarify the number of electrons transferred.

It has been shown how the excess molybdenate ions remaining in a film can have an unpredictable and potentially deleterious influence on the system's dielectric properties. This is a difficult problem to eliminate owing to the large size of the anion making it more easily trapped in the polymer matrix.

Phosphomolybdic acid in THF shows a rich electrochemistry. A pair of quasi-reversible waves appear in the cyclic voltammetry in the vicinity of 0.4 and 0.6 V vs. SCE. The potential of these redox transitions depends upon solution pH.

## 5 Future Work

One crucial area for future exploration is the replacement of PMA with some other oxidant. The problems associated with residual trapped ions are unambiguous. Further issues arise from this particular material. In its solid state, PMA exists as a hydrate. We found that the PMA we received contained between 30 and 40 water molecules per molecule of the

oxidant. This water is released into the solvent when the crystals are dissolved in THF. It is possible that the excess water has a number of deleterious consequences. Firstly, the polymerization mechanism involves a reactive radical cation intermediate. This radical could react with stray water (or any other nucleophile) leading to undesired side-products and premature chain termination. Secondly, in order to be conducting, the fully-formed polymer backbone must contain radical cation charge carriers. Again, these are prone to attack by nucleophiles such as water, which leads to disruption of the conjugation, and hence loss of conductivity [19] in the polymer. One premise of this composite project is that the polyurethane host matrix will serve as a barrier to atmospheric moisture; this is perhaps not very helpful if the matrix itself is wet. Thirdly, water and THF are generally miscible, but if the water becomes loaded with ions (such as PMA), it will form a separate phase. This phase separation could explain the settling of PMA in the sample preparations with increased oxidant content. It is also consistent with observations that such preparations often produced a sticky residue in the bottom of the casting dish. The residue has not been thoroughly examined, but that product may have been caused by water.

One approach might be the careful removal of water from the THF+PMA solution with a drying agent such as magnesium sulfate. A preliminary examination of such a process was undertaken by Mossman [14]. However, Eqs. 5–7, Table 1, and Figure 7 indicate the sensitivity of the PMA redox potentials to acidity. In an anhydrous environment, the acidity of the protons released by monomer coupling may be unclear, and hence the redox potentials of the phosphomolybdenate species may behave unpredictably.

Consequently, a better oxidant could be selected. Since it is clear that residual ions are a problem for the PMA reaction, and it is likely that the high degree of crystal hydration leads to problems, replacement of PMA is in order. For the current system, an oxidant with a formal potential in the 0.4 V range should be adequate. Ferrocenium hexafluorophosphate might be a reasonable choice. Ferrocene is usually electrochemically well-behaved, transferring one electron with good kinetics in organic media. It is anhydrous, and any residual counterions left in the film would be  $\text{PF}_6^-$ , an electrochemically inert species. Furthermore, ferrocenium reduction is not proton-dependent, alleviating the problem of PMA redox potential dependency on solution pH.

# Symbols and Abbreviations

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$\Delta E_p$ : Peak potential separation;  $\Delta E_p = E_{pa} - E_{pc}$

$\epsilon$ : Permittivity

$\epsilon_c$ : Permittivity of a composite

$\epsilon_f$ : Permittivity of a filler

$\epsilon_m$ : Permittivity of an unfilled host matrix

$v$ : Voltage sweep rate

$\sigma$ : Conductivity

$\rho_f$ : Density of the filler

$\rho_m$ : Density of the matrix

$\phi$ : Fraction of filler;  $0 \leq \phi \leq 1$

$\phi_C$ : Percolation threshold

$\phi_v$ : Volume fraction of filler

$\phi_w$ : Weight fraction of filler

$E_{1/2}$ : Half-wave potential

$E_{pa}$ : Potential of the anodic current peak

$E_{pc}$ : Potential of the cathodic current peak

$j$ : Current density (current per unit area of electrode surface)

$j_{pa}$ : Anodic peak current density

$j_{pc}$ : Cathodic peak current density

**DEA**: Dielectric Analysis or Dielectric Analyzer

**PMA**: Phosphomolybdic acid

**SCE**: Saturated calomel electrode

**THF**: Tetrahydrofuran

**TIF**: Technology Investment Fund

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Freund's method for cascade polymerization is proving to be a versatile method to produce conducting polymers in a processible manner. One promising avenue for this technology is the creation of composite materials which consist of a interpenetrating network of conducting polymer inside an inert host matrix. Our early work with these composites is showing that they can offer a number of unusual properties.

This paper focuses on clarifying the nature of the oxidant used to date, phosphomolybdic acid (PMA), and its role in the process. Polypyrrole-polyurethane composites of varying loading levels were made and their permittivity measured, with percolation occurring near 4% v/v. The ratio of pyrrole monomer to oxidant was varied over a range from 12:1 to 1:2. Insufficient oxidant led to incomplete polymerization and hence poor permittivity. Excess oxidant left trapped ions in the composites which led to secondary dielectric effects. A ratio of around 2.5:1 appears to be a reasonable compromise.

The cyclic voltammetry of PMA in tetrahydrofuran reveals a pair of quasi-reversible waves near 0.4 V and 0.6 V vs. SCE. The position of these waves is pH-dependent.

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