I. POLYMER FILMS FOR HIGH TEMPERATURE CAPACITOR APPLICATIONS

II. DIFFERENTIAL ELECTROCHEMICAL MASS SPECTROMETRY

by

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List of Common Abbreviations

BDS – broadband dielectric spectroscopy
BOPP – biaxially oriented polypropylene
D-E loop – a plot of electric displacement D vs. applied electric field E
DSC – differential scanning calorimetry
HEV – hybrid electric vehicle
HTPC – high temperature or high Tg polycarbonate
LDPE – low density polyethylene
MLF – multilayer film
P(VDF-HFP) – poly(vinylidene fluoride-co-hexafluoropropylene)
P(VDF-TFE) – poly(vinylidene fluoride-co-tetrafluoroethylene)
PB – phosphate buffer
PC – polycarbonate
PEEK – poly(ether ether ketone)
PEN – poly(ethylene naphthalate)
PET – poly(ethylene terephthalate)
PI – polyimide
PPS – poly(phenylene sulfide)
PSF – polysulfone
PVDF – poly(vinylidene fluoride)
RHE – reversible hydrogen electrode
T_g – glass transition temperature
I. Polymer Films for High Temperature Capacitor Applications

II. Differential Electrochemical Mass Spectrometry

ABSTRACT

by

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Polycarbonate (PC)/poly(vinylidene fluoride) (PVDF) multilayer films (MLFs) with normal PC and high temperature PC (HTPC) were studied with broadband dielectric spectroscopy (BDS), electric displacement-electric field (D-E) loop, leakage current, and breakdown measurements to determine their high temperature performance and loss mechanism. The MLF containing HTPC performed better, which is attributed to its higher glass transition temperature (T_g), better maintaining interfacial polarization and providing a “blocking electrode” preventing charge carrier injection from PVDF into PC.

Twelve (12) new polyimides (PIs) with nitrile (CN) groups attached to the polymer main chains were studied with BDS and D-E loop measurements. A ratio of experimental and theoretical dipolar polarization was calculated to estimate how easily the CN dipoles could rotate in response to the external electric field. Experimental results show that adding polar groups to PIs increased the permittivity but dielectric loss increased too because the dipoles in the rigid PI structures were difficult to rotate.

An online mass spectrometry probe was developed for the detection of volatile reaction products and intermediates of electrochemical reactions in an
aqueous solution. A wall-jet configuration was used to produce a laminar flow of electrolyte on the surface of a solid Au electrode in the center of the probe. The mass spectrometric ion current correlated well with the hydrazine oxidation current.
PART I

CHAPTER 1

High Temperature Polymer Capacitor Films

INTRODUCTION

Since the society is becoming increasingly aware of the climate change caused by burning fossil fuels, there is an increasing demand for environmentally more friendly and fuel efficient electric and hybrid electric vehicles (EV and HEVs).[1] Because of increasing competition, manufacturers strive to lower the prices of every component in a car, especially EV and HEVs.

HEVs use several large capacitors in their power electronics circuits.[2] For the HEV purposes, the weight, volume and cost of the capacitors are critical. In addition, these so-called DC-link power capacitors have to operate under harsh conditions of extreme temperatures and, as part of an HEV, last the lifetime of the vehicle. DC-link capacitors must also accept high ripple currents, 80 A_{rms} at a frequency of 20 kHz and operate at temperatures up to 150 °C.[1][3]
All these requirements leave only a small number of capacitor types which fit this purpose. Out of the commercially available capacitors, polymer film capacitors are highly favored in HEV power electronics[4] because of their high dielectric breakdown strength[5], low dielectric losses[6], and self-healing property[7], which precludes catastrophic failures. The above-mentioned advantages also make polymer film capacitors desirable in some military and aerospace applications, especially if they can operate at very high temperatures and have high energy densities.[8]

The most popular film capacitor is the biaxially oriented polypropylene (BOPP) film capacitor. BOPP has a very low dielectric loss and a high breakdown strength at temperatures up to 85 °C.[7] Above that temperature, its performance starts to degrade. As another shortcoming, BOPP has a relatively low dielectric constant of 2.25, which makes BOPP capacitors bulky, and also more expensive because of higher material and processing costs.

1.1. In Search for High Temperature Polymer Film Capacitor Materials

There are some other materials available that can work at significantly higher temperatures than BOPP, such as poly(ethylene naphthalate) (PEN), poly(ethylene terephthalate) (PET), poly(phenylene sulfide) (PPS), and poly(ether ether ketone) (PEEK). However, these material have their own limitations. PEN cannot be used at higher frequencies (1000 Hz and above) because of very high dielectric losses.[9] PET only finds limited use in power
electronics because of its high losses at higher temperature and frequency. PPS and PEEK are prohibitively expensive, even though their dielectric losses at high temperatures (around 150 °C) are low. Also, PEEK has generally low breakdown strength resulting in low energy density.[7]

In conclusion, there is currently no good commercial polymer film that could operate at higher temperatures (150 °C), as well as have a high energy density with low losses,

1.2. Blending Polymers to Improve Properties

Attempts have been made to combine materials with complementary properties to make new materials with enhanced properties. Poly(vinylidene fluoride) PVDF has a high dielectric constant ($\varepsilon_r=12$), but it also has a high dielectric loss due to its ferroelectric property.[10] Polycarbonate (PC), on the other hand, has very low dielectric loss.[11] However, an immiscible blend of the two shows a significantly decreased dielectric performance as compared to its constituents.[12]

1.3. Multilayer Films

At Case Western Reserve University (CWRU), microlayer coextrusion of polymer films was developed.[13] It allows to combine the complementary advantageous properties of different polymers, to produce multilayered structures
with enhanced mechanical, dielectric,[12, 14-20] and optical[21, 22] properties. The coextrusion enables the combination of 2 or 3 polymers in an ABABABAB (or ABCBABCBA)[13] fashion into 2 to 4096 layers, yielding a minimum layer thickness of ca. 10 nm. Figure 1.1 shows a schematic of the microlayer coextrusion equipment. Two different polymer resins are added, one into extruder A and the other into extruder B. The resins are melted and forced through a two-layer feedblock into layer multipliers that determine the number of layers in the multilayer film (MLF). The flow of melted polymers then exits the exit die and is stretched in the direction of exit, onto a cooled drum.

![Schematic of multilayer coextrusion process](image)

**Figure 1.1.** Schematic of the multilayer coextrusion process [23].

The MLFs exhibit a number of improved dielectric properties comparing to their constituent polymers. PVDF has high permittivity and high dielectric loss as can be seen from the broad $D-E$ loop in Figure 1.2. PC has low permittivity and

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*Please see Part I, Chapter 3 of this dissertation if you would like to learn more about D-E loops.*
low dielectric loss as seen from the narrow $D$-$E$ loop in Figure 1.3. When PVDF and PC are combined in an MLF (see Figure 1.4), the dielectric loss is reduced drastically, almost to the level of the PC and the permittivity of the MLF is significantly higher than that of the PC.

These results can be explained as follows. The nominal electric field in PVDF is lower, due to its high permittivity ($\varepsilon_r=12$), and higher in PC because of its low permittivity ($\varepsilon_r=3$), as seen in Figure 1.5. In order to explain this further, we first need to understand how ferroelectric hysteresis works.[24] PVDF is partly crystalline, often with a mixture of $\alpha$, $\beta$, $\gamma$ and $\delta$ phases. Some of these crystals ($\beta$, $\gamma$, and $\delta$) contain a polar unit cell with a net dipole moment. As a result, spontaneous polarization results in the sample when large domains are formed. Switching (or changing direction) of the spontaneous polarization (via switching of ferroelectric domains) leads to a broad ferroelectric hysteresis loop, where the remaining polarization at zero field is called the remanent polarization ($P_r$) and the electric field at zero polarization is called the coercive field ($E_c$). Ferroelectric switching is absolutely undesired for film capacitor applications. In addition to crystalline dipoles and domains, PVDF also has 50% amorphous dipoles, which is the paraelectric state without any ferroelectric domains. It is these amorphous dipoles that raise the permittivity of the MLF in Figure 1.4 above the permittivity of neat PC.
Figure 1.2. Continuous $D$-$E$ loops of a PVDF film ($\alpha$ phase; 10 µm) at room temperature. The poling electric field is a sinusoidal wave with a frequency of 10 Hz.
Figure 1.3. Continuous $D$-$E$ loops of a PC film (10 µm) at room temperature. The poling electric field is a sine wave with a frequency of 10 Hz.
Figure 1.4. Continuous $D$-$E$ loops of PC, PVDF and the PC/PVDF 70/30 33-layer MLFs at room temperature. All films are about 10 µm thick. The poling electric field is a sine wave with a frequency of 10 Hz.
1.4. Interfacial Polarization in MLFs

In addition to lowering the dielectric loss, there is another beneficial effect from multilayering, called *interfacial polarization* that further improves the insulating properties of the MLFs. When two materials with different conductivities and dielectric constants are put in contact, charges (electrons/holes or ions) will accumulate at the interface of the two materials, when an external electric field is applied. This interfacial charge accumulation is referred to as the Maxwell-Wagner-Sillars interfacial polarization[25]. When an
external electric field is applied across the MLF, charge carries, especially in the more conductive PVDF, will migrate and accumulate at the PC/PVDF interfaces, but cannot pass from PVDF to PC, due to much lower electronic and ionic conductivities of PC (Figure 1.6). These interfacial charges serve as effective traps for external electrons injected from metal electrodes, and they tend to lower the DC conductivity and dielectric losses for MLFs and increases the breakdown strength.[16, 17]

**Figure 1.6.** A schematic representation of the interfacial polarization in a PC/PVDF MLF under an external poling electric field.

In addition to the PC/PVDF MLFs, several other MLF system have been studied as well.[12, 18, 20]
1.5. How to Create MLFs That Can Outperform BOPP?

The most powerful aspect of the MLF technology is that it provides an avenue to create new and better materials by combining (with some limitations) different polymers with complementary properties. For example, if there is a PC with a high glass transition temperature ($T_g$), it could be used in combination with PVDF to produce MLFs that can perform at higher temperatures. Fortunately, such PCs exist and PART I, Chapter 4 of this dissertation is devoted to the study of an MLF composed of PVDF and a high $T_g$ PC (HTPC), comparing it with an MLF composed of PVDF and normal PC. In dielectric breakdown testing, the MLF with the HTPC outperformed BOPP, normal PC, MLF with the normal PC, and PVDF.

1.6. Very High Temperature Materials - Polyimides

The MLFs investigated so far mostly consisted of PVDF (or its copolymers) and PC, polysulfone (PSF), or PET. None of these materials can perform higher than 160-170 °C. What if we desired something that could go above 200 °C and have high energy density and low loss at the same time? This is a difficult assignment. We should begin with a material that is already high-temperature resistant. These must be materials with very high $T_g$. Since $T_g$ entails the long range segmental motion of the polymer chains, having a high $T_g$ requires a polymer chain that is rigid and resistant to cooperative motion of
segments. Such chains often consist of aromatic rings. A good example is polyimides, known for their rigid backbone structure that results in a very high $T_g$ and high temperature performance. However, the issue is that polyimides have generally low permittivity.[26] Of course, when the temperature is raised close to or above the $T_g$, permittivity increases but so does dielectric loss because the long-range segmental motions of the polymer chains begin. Therefore, it is better to stay below the $T_g$.

If we desire high permittivity, high temperature, and low losses, then we need to pick materials with the following properties. First, the material should have a very high $T_g$. It should include dipolar groups with a high dipole moment, and there must be enough free volume for those groups to freely rotate under an applied electric field. Therefore, we need to look for materials that contain small dipolar groups that can spin or flip in an applied electric field and relax back quickly when the field is removed. These materials could be identified with broadband dielectric spectroscopy (BDS) (see PART I, Chapter 3 of this dissertation for more on BDS) because they would exhibit sub-$T_g$ relaxations as a result of those dipolar groups turning in an applied electric field.[27]

In this dissertation, PART I, Chapter 5 is devoted to the investigation of polyimides that contain such polar nitrile (-CN) groups attached to the polymer main chain.
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2.1. The Working Principles of Capacitors

First, let us look at in general how a capacitor works. The simplest capacitor is a parallel plate capacitor consisting of an non-conducting material (a.k.a. a dielectric) sandwiched between two metal plates as shown in Figure 2.1.

![Schematic of a simple parallel plate capacitor](image)

**Figure 2.1.** Schematic of a simple parallel plate capacitor.

Since capacitors are energy storage devices, let us first see what determines how much electric charge is stored in a capacitor, such as the one shown in Figure 2.1. The capacitance $C$ of a parallel plate capacitor is given by:
\[ C = \frac{\varepsilon_0 \varepsilon_r A}{d}, \quad (2.1) \]

where \( \varepsilon_0 \) is a fundamental constant known as the electric constant or, permittivity of vacuum: \( \varepsilon_0 = 8.85... \times 10^{-12} \frac{F}{m} \), and where \( \varepsilon_r \) is the relative permittivity of the dielectric material such that \( \varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \), where \( \varepsilon \) is called the permittivity. \( A \) is the area of the plate and \( d \) is the distance between the metal plates (or the thickness of the dielectric).

The energy \( W \) that a capacitor holds is given by

\[ W = \frac{CU^2}{2}, \quad (2.2) \]

where \( U \) is the voltage applied between the metal plates.

Let us now look at what happens when a voltage source with is connected to the capacitor plates with nothing (only vacuum) between the plates (Figure 2.2a). The metal plates become oppositely charged and the charges give rise to an electric field \( E \) between the plates: \( E = \frac{V}{d} \). The field remains even after the voltage source is removed because the charges have nowhere to go (Figure 2.2b). Now let us place a dielectric (green) between the charged plates and let us begin denoting the electric field due to the charged plates as \( E_0 \) instead of \( E \) (Figure 2.2c). At the first instant after insertion of the dielectric, nothing happens to the dielectric but after a very short period of time, charges appear on the opposing faces of the dielectric (Figure 2.2d). The appearance of those charges is known as polarization of the dielectric. The polarization charges give rise to an electric field \( E' \) (Figure 2.2e) that points opposite to the applied field \( E_0 \).
According to the superposition principle of electric fields, the total field \( E \) (red arrow in Figure 2.2f) in the dielectric will be the vector sum of \( E_0 \) and \( E' \), and since \( E_0 \) and \( E' \) are antiparallel, \( E = E_0 - E' \). Thus we see that polarization reduces the electric field produced by the charges on the metal plates.

![Figure 2.2. Development of polarization in a dielectric.](image)

Based on the above discussion, we can define some important quantities for the research of dielectrics. The relative permittivity \( \varepsilon_r \) of a dielectric shows how much the electric field \( E_0 \), produced by the charges on the metal plates, is weakened by the polarization of the dielectric.

\[
\varepsilon_r = \frac{E_0}{E}
\]  

(2.3)
\( \varepsilon_r \) is thus an intrinsic property of the dielectric material.

Another important quantity, electric displacement \( D \), which is equal to the charge density (C/m\(^2\)) on the metal plates, is defined as \( D = E_0 \varepsilon_0 \). The actual electric field in the dielectric depends on the voltage across the metal plates and the distance between the plates and is given by

\[
E = \frac{V}{d}.
\] (2.4)

### 2.2. Mechanisms of Polarization in Dielectrics

Now, as we saw earlier, the energy that a capacitor contains, is determined by the voltage and the capacitance. Obviously we want to maximize the amount of energy a capacitor stores without increasing its mass or volume. According to equation (2.2) there are two ways of doing that: i) increasing the voltage \( U \) and ii) increasing the relative permittivity \( \varepsilon_r \). However, there is a maximum voltage that can be applied across a capacitor before it experiences a dielectric breakdown. For a dielectric material, there is a certain maximum electric field \( E_{\text{max}} \) above which there will be a spark through the dielectric (akin to lightning) and a hole will be burned through the material possibly destroying or short-circuiting the capacitor. This \( E_{\text{max}} \) is called the breakdown field or the dielectric strength of the material.

At this point we are more interested in increasing the energy density (energy stored per unit volume) by increasing \( \varepsilon_r \). This means increasing the
polarization produced at a given voltage. So, let us look at how polarization occurs. There exist 5 types of polarization (see Figure 2.3) in the order of decreasing initiation frequency: electronic, atomic (or vibrational), dipolar (or orientational), ionic, and interfacial polarization. The polarizations occur through the following mechanisms.

**Electronic polarization** ($P_e$) – deformations in the electron cloud with respect to the nucleus in atoms or molecules under an external electric field. $P_e$ begins at optical frequencies and usually contributes about 2 or 3 units to $\varepsilon_r$.

**Atomic polarization** ($P_a$) – stretching and bending of interatomic covalent bonds. Begins at infrared frequencies and contributes only a fraction (0.1-0.5) of $P_e$ to $\varepsilon_r$.

**Dipolar polarization** ($P_{dip}$) – molecular dipoles (e.g., polar bonds) trying to orient along an external electric field. Begins at radio frequencies and can contribute to $\varepsilon_r$ up to 1 or 2 orders of magnitude more than $P_e$.

**Ionic polarization** ($P_{ion}$) – ions accumulating at phase boundaries due to the applied electric field. Begins below 100 or 10 Hz and can contribute to $\varepsilon_r$ more than $P_{dip}$.

**Interfacial polarization** ($P_{int}$) – charge carriers accumulating at phase boundaries due to different dielectric constants and conductivities of two phases. Occurs at very low frequencies and can contribute to $\varepsilon_r$ as much or more than $P_{dip}$.

Dipolar polarization is of the most interest to us because it can contribute vastly to $\varepsilon_r$ and it can be brought about by introducing dipoles into the structures.
of molecules. Also, dipolar polarization occurs fast enough, compared to ionic and interfacial polarization, so it can be used in dielectric capacitors that require fast charging and discharging.

**Figure 2.3.** Different types of polarization as a function of frequency. The top panel shows molar polarization and the bottom panel shows the dissipation.[1]

### 2.3. Dielectric Loss

So far, we have established that we should design or study materials that contain dipoles in their molecular structure, since dipoles can give a huge boost to the permittivity. However, there is another quantity that is of importance:
dielectric loss. What exactly is dielectric loss? Let us illustrate this with a simple example: you drop a ball with a mass $m$ from a height $h$, it bounces up from the ground but now to a smaller height $h_1$. In this case the total potential energy of the ball before it was dropped was: $mgh$ and its potential energy after the drop, when reaching height $h_1$ and stopping for a brief moment, was $mgh_1$. If the ball had been ideally elastic, $h$ would be equal to $h_1$ but since some of the energy of the drop went into producing heat, $h_1 < h$ and the energy that went into producing heat is $Q = mgh - mgh_1$ and this is the energy that was lost. In dielectrics loss can be described in a very similar way. If we put a certain amount of energy into charging a capacitor, then we are not going to get back the same amount of energy when we discharge the capacitor. What we get back is a little bit less and the difference is called the dielectric loss, denoted as $\varepsilon''$. There is also a term called the dissipation factor, denoted as $\tan \delta$ which is simply the loss divided by the energy that was initially put into the capacitor. Mathematically,

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$  \hspace{1cm} (2.5)

where $\varepsilon'$ is the real part of the permittivity $\varepsilon$ which itself is actually a complex number so that

$$\varepsilon = \varepsilon' - j\varepsilon''$$  \hspace{1cm} (2.6)

It is crucial to reduce dielectric loss in capacitors because loss produces excess heat. Even a 0.1% loss per charge/discharge cycle, meaning 99.9% of the energy that was put into the capacitor can be withdrawn, can be a problem. Assume we have a 1000 µF DC-link capacitor (in an electric vehicle) with a
voltage rating of 1000 V. This means, when fully charged, it would contain 500 J
of energy according to \( W = \frac{CU^2}{2} \). Now 0.1% of that is 0.5 J. But if the capacitor
works at a frequency of 10 kHz, a frequency commonly used in electric car power
electronics, 0.5 J per cycle would translate into 5 kW which is a lot for a 4 l
capacitor to dissipate. The capacitor will heat up and the dielectric loss will
increase at higher temperatures, leading to a catastrophic thermal runaway.

REFERENCES

CHAPTER 3

Dielectric Measurements

3.1. Broadband Dielectric Spectroscopy (BDS)

The BDS spectrometer allows us to determine the dielectric constant $\varepsilon_r$ and the dielectric loss $\varepsilon_r''$ of materials. It does so by applying an AC voltage across a tiny capacitor that contains between its plates the material we are studying. The core part of the instrument is a frequency response analyzer which consists of two main parts: an AC signal generator that produces an AC voltage $U(t) = U_{\text{max}} \sin(\omega t)$ at various frequencies, and a correlator which measures the in-phase and quadrature (90° out of phase) components of the current with respect to the output of the AC generator[1]. The correlator multiplies its input signal with sine and cosine reference signals from the generator and then integrates the product over a specified number of cycles. This process is described in more detail below.
Figure 3.1. The relationship between charging current $I_c$ and loss current $I_L$. (a) equivalent circuit; (b) complex plane showing the charging and loss current; (c) charging and loss current densities $J_C$ and $J_L$, relating the dielectric quantities $\varepsilon'$ and $\varepsilon''$. Care must be taken because here $\varepsilon'$ and $\varepsilon''$ are absolute (i.e. not divided by $\varepsilon_0$).

Any dielectric sample can be represented by the equivalent circuit in Figure 3.1(a) [2]. It consist of a capacitor $C$ in parallel with a resistor with conductance $G$, and a voltage source $U$. As can be seen from Figure 3.1(b), the loss current $I_L$ is in phase with the applied voltage $U$ whereas the charging current $I_C$ is $90^\circ$ out of phase. The amplitude $I_{max}$ and phase $\varphi$ (relative to the applied AC voltage $U$) of the resulting current is recorded. By the way, in dielectrics $\varphi$ is referred to as the phase angle. If the applied voltage is $U(t) = U_{max} \sin(\omega t)$ and the resulting current is $I(t) = I_{max} \sin(\omega t + \phi)$, then in order to get the in-phase and out-of-phase components of the current, the Fourier coefficients are calculated. It is known from trigonometry that

$$\sin(\alpha + \beta) = \sin \alpha \cos \beta + \cos \alpha \sin \beta.$$  \hspace{1cm} (3.1)
Therefore, we can write:

$$\sin(\omega t + \phi) = \sin(\omega t)\cos \phi + \cos(\omega t)\sin \phi. \quad (3.2)$$

Let us substitute

\[
a = \sin \phi \\
b = \cos \phi.
\]  \quad (3.3)

Then we get

$$\sin(\omega t + \phi) = a \cos(\omega t) + b \sin(\omega t). \quad (3.4)$$

Now, drawing on the above, for the purposes of the Fourier series, it is assumed that the resulting current is a sum of sinusoidal functions such that:

$$I(t) = a \cos\left(\frac{2\pi t}{T}\right) + b \sin\left(\frac{2\pi t}{T}\right), \quad (3.5)$$

where T is the period and we used the relation \( \omega = \frac{2\pi}{T} \).

The Fourier coefficients \( a \) and \( b \) can now be calculated as:

\[
a = \frac{2}{T} \int_0^T I(t) \cos\left(\frac{2\pi t}{T}\right) dt \\
b = \frac{2}{T} \int_0^T I(t) \sin\left(\frac{2\pi t}{T}\right) dt.
\]  \quad (3.6)

From here, because of the substitution in Eq. (3.3), we can infer the dissipation factor: \( \tan \delta = a/b \). Also, since the sample area, thickness, frequency and amplitude of the applied voltage, and amplitude of the resulting current are known, we can now calculate \( \varepsilon' \) and \( \varepsilon'' \), relying on the relations shown in Figure 3.1.

In BDS the frequency of the applied voltage is varied and the dielectric parameters of the sample are measured, yielding useful information about the
polarization (also called relaxation) processes in the material giving insights to molecular-level structure and processes. An example of a BDS spectrum is shown in Figure 3.2.

![Calibre/Solef](image)

**Figure 3.2.** $\varepsilon_r^\prime$ vs. $f$ spectrum for a polymer film with various relaxation peaks identified.

3.2. Electric Displacement-Electric Field ($D$-$E$) Loop Measurements

While BDS measurements are usually done at low fields (e.g. 0.02 MV/m) due to technical limitations of producing high frequency high voltage signals, another analysis method is used to characterize materials under high electric fields (e.g. 500 MV/m). In $D$-$E$ loop measurements, similarly to BDS, a sinusoidal
voltage signal is applied across the sample capacitor and the current is measured and integrated at each point, and the resulting charge is divided by the sample area to yield the electric displacement $D$. $D$ is then plotted against the field $E$, yielding loops such as the one shown in Figure 3.3.

![Figure 3.3. D-E loop from a polymer film (PC/PVDF 70/30 33L) at 150 °C, applying a sinusoidal voltage with a frequency of 10 Hz.](image)

An equivalent circuit (Figure 3.4) can be used to describe the different polarization processes in dielectric samples. Purely capacitive behavior can be modeled as a capacitor in an equivalent circuit. Materials also exhibit ionic conduction which is modeled as a capacitor in series with a resistor here. Finally, samples can have electronic conductivity, which is represented with a
resistor. The slope of a D-E loop is used for calculating the permittivity of the material from

$$\varepsilon_r = \frac{D}{\varepsilon_0 E}$$ \hspace{1cm} (3.7)

The energy released from the capacitor can be calculated by integrating the D-E loop:

$$W = \int E \, dD$$ \hspace{1cm} (3.8)

Simulated D-E loops (Figure 3.5), based on the equivalent circuit in Figure 3.4, can be used to understand the dielectric loss mechanisms. An ideal, lossless capacitor is represented by the blue line. Electronic conduction upshifts the upper half of the D-E loop, as shown by the green curve, and ionic conduction broadens the loop symmetrically about the x-axis (magenta curve). The red curve is the sum of the three curves and should resemble experimental data.

Also, D-E loops can show field dependence of the polarization processes because some materials (e.g., ferroelectrics) only exhibit dipolar polarization above the coercive field $E_C$. 


Figure 3.4. Equivalent circuit describing a dielectric sample. Capacitor C0 represents the purely capacitive component, resistor R1 and capacitor C1 together represent ionic conduction and resistor R2 represents the electronic conduction.

Figure 3.5. Simulated $D$-$E$ loops showing the different processes in a dielectric material. $f=10$ Hz.
REFERENCES


CHAPTER 4

PC/PVDF Multilayer Films for High Temperature Capacitor Applications

ABSTRACT

Microlayer coextruded polycarbonate (PC)/poly(vinylidene fluoride) (PVDF) 33-layer multilayer films (MLFs) with a PC/PVDF ratio of 70/30 (vol./vol.) were studied using broadband dielectric spectroscopy (BDS), electric displacement-electric field ($D$-$E$) loop, DC leakage current, and dielectric breakdown measurements to determine the potential for high temperature film capacitor applications. Two PCs were used in the MLFs: a normal bisphenol A PC (BPA-PC) and a high glass transition temperature ($T_g$) PC (HTPC). The MLF containing the HTPC exhibited higher breakdown strength, reduced dielectric loss, and lower DC conductivity than that containing the normal PC. An interfacial polarization model is proposed to explain this observation: the highly insulating PC layers serve as “blocking electrodes” for both electrons and ions in the relatively conductive PVDF. After electric polarization, the polarized charge carriers accumulate at the PC/PVDF interfaces, which tends to decrease the leakage current. Our experimental results suggested that HTPC was a better “blocking electrode” than normal PC due to its higher $T_g$. The higher interfacial
polarization in the HTPC/PVDF MLFs decreased leakage current and thus enhanced dielectric properties at high temperatures.

INTRODUCTION

Capacitors are used in every electronic device from computers to cell phones and power electronics in hybrid electric vehicles (HEVs)[1], utility power systems and military applications. In there they fulfill functions such as signal coupling and decoupling[2], power conditioning, DC-to-AC conversion in HEVs and renewable energy sources[3], and as pulsed power sources[4].

There is an increasing demand for cheap, compact and highly reliable high power capacitors for HEVs, wind turbines, solar cells, and fuel cells as the society is pushing for reduced greenhouse gas emissions and automotive manufacturers strive for more fuel efficient vehicles.

HEVs use DC-link capacitors in the DC-to-AC and AC-to-DC power conversion. These DC-link capacitors must supply periodic high currents, last more than 10 years, and be able to accept high ripple currents[5]. There are only two types of capacitors that can fulfill these requirements: electrolytic and polymer film capacitors.

Despite a higher energy density (2 J/cm³), electrolytic capacitors have lower maximum voltage than polymer film capacitors, cannot accept high ripple currents, and have shorter lifetime due to electrolyte dry-out which results in shorting and possibly in catastrophic failure. Polymer film capacitors, on the other
hand, due to their low internal resistance, can accept very high ripple currents[3], have a longer lifetime, and are more reliable than electrolytic capacitors in critical applications[6], especially under more extreme conditions[7] because they fail gracefully due to self-healing[8].

In addition to the above, polymer films are easy to manufacture and process on a large scale. They have excellent electrical insulation properties, high dielectric breakdown strength[9] and low dielectric loss[10].

The state-of-the-art polymer film capacitor has long been the biaxially oriented polypropylene (BOPP) capacitor. It has a very low dissipation factor of 0.0004 at room temperature[6], and a high breakdown strength of more than 700 MV/m[6]. Unfortunately, BOPP begins to decline in performance above 85 °C and cannot be used above 105 °C[6] whereas it would be desirable for HEV power electronics to have capacitors working between 120 and 130 °C[5]. Also, BOPP capacitors are bulky because of its low dielectric constant of 2.25 and thus more expensive than electrolytic capacitors of equal parameters such as capacitance[5].

At CWRU we have developed a new type of dielectric polymeric material, multilayer films (MLFs), that can perform as well as, or better than BOPP, and can operate at much higher temperatures, up to 150 °C. The MLFs are produced by microlayer coextrusion, allowing the combination of 2 or 3 polymers in alternating layers, creating films containing 2 to 4096 layers with layer thicknesses as thin as 10 nm[11]. Polymers with complementary properties such as high dielectric strength and high dielectric constant can be thus combined to
produce materials with novel properties, better than the individual constituents. One such material, composed of alternating layers of a high breakdown strength material [polycarbonate (PC)] and a high dielectric constant material (poly(vinylidene-co-hexafluoropropylene), [P(VDF-HFP)]), was studied by Mackey et al., and it was found to have significantly higher breakdown strength than either of its individual constituents[12].

In addition, other studies [13, 14] found that MLFs with thinner layers of PVDF interleaved with PC exhibited less hysteresis loop loss. This could be explained by the fact that the electric field in the PVDF layer is much weaker, due to its high dielectric constant (ε_r=12), than in the PC layer (ε_r=3). It is known that a coercive field (E_C) of about 70 MV/m is required to switch β crystalline dipoles in PVDF crystals, and this ferroelectric switching is the source of hysteresis loop loss. If the field is below E_C, loop losses are minimized. However, the authors found that the D-E hysteresis loop loss was not due to ferroelectric dipole switching but due to ion migration caused by the applied electric field in the PVDF layers. When an electric field is applied, ions of opposite signs migrate to the PC/PVDF interfaces. The migration will stop when the diffusion current and electrostatic repulsion (both working against the migration current) reach an equilibrium with the migration current. In thinner PVDF layers, charge buildup is weaker, and will reach an equilibrium faster because of smaller travel distances for the ions. This will reduce the hysteresis loop losses and allow ions to relax back faster, increasing the overall output energy density of the MLF capacitor. It
was found that PVDF layer thicknesses above 300 nm will cause extra ion migrational loss as the layer thickness increases[14].

However, there is a limit to how thin the PC layers can be before DC conduction loss increases. It was proposed[15] that mobile space charges in PVDF (i.e., ions, electrons, or both, depending on the temperature) that accumulate at the polysulfone (PSF)/PVDF interfaces in MLFs can give rise to Maxwell-Wagner-Sillars interfacial polarization. These interfacial charges will actually prevent further flow of charge carriers across the interfaces. In other words, these charges at the interfaces act as charge-blocking or trapping layers for conduction of electrons. However, if the PSF layers in the MLF are too thin, charge carriers are allowed to pass through them, making the MLF more conductive. Lower breakdown strength, shorter lifetime, and higher DC conductivity are observed if the PSF layers become too thin (<200 nm). Optimal thickness of >200 nm for the PSF (or PC) layer and <300 nm for the PVDF layer is suggested to achieve the best dielectric performance in terms of high breakdown strength, high energy density, and low loss.

In addition to the layer thickness, stretching can also influence the dielectric properties of MLFs. Carr et al.[16] showed that if the PET/P(VDF-TFE) MLF is biaxially stretched after extrusion, it will have a higher dielectric constant, a significantly higher breakdown strength and nearly double the energy density at breakdown. It was found that biaxial stretching orients the P(VDF-TFE) crystals on edge, setting the P(VDF-TFE) chain axes parallel to the layer plane, and the dipoles in a plane parallel to the applied electric field. This resulted in a more
efficient amorphous (not crystalline) dipole switching and thus a higher dielectric constant and energy storage. Since the Maxwell-Wagner-Sillars interfacial polarization depends on the dielectric constants of the two phases in contact, a higher dielectric constant contrast resulted in a higher interfacial polarization, leading to more charge buildup at the PC/PVDF interface and eventually a higher breakdown strength.

In conclusion, layered polymer structures have benefits in preventing ferroelectric dipole switching and (impurity) ion conduction loss by confining charge carriers into the PVDF layers, while building up interfacial charged layers that block further flow of charge carriers, which significantly decreases dielectric losses and increases breakdown strength.

In this work we have compared two MLF systems, PC/PVDF and HTPC/PVDF (where HTPC is a high T_g PC) at high temperatures. The high T_g of HTPC enhanced the breakdown strength of the MLFs and reduced dielectric loss. It is proposed that better interfacial polarization improved the breakdown strength and reduced DC conduction of MLFs. It is found that PVDF injects charge carriers into PC when the two are in contact and the injection is easier as the temperature is approaching the T_g of the PC. To mitigate this problem of charge injection, it is proposed to make the film layer adjacent to the metal electrode out of a high k material to reduce the field emission of electrons from the cathode into the polymer. A possible candidate for such a material is Al_2O_3 which has a high k as PVDF but is not susceptible to electrochemical reactions.
EXPERIMENTAL

4.1. Film Manufacture and Preparation for Dielectric Characterization

Poly(vinylidene fluoride) (PVDF) homopolymer Solef® 6010 from Solvay Plastics, polycarbonate (PC) CALIBRE™ 200-6 from Styron (now Trinseo), and PC Apec® 1745 from Bayer MaterialScience were used to produce two MLFs: Apec/Solef and Calibre/Solef, and the controls (one-component films) Apec, Calibre and Solef. Commercial capacitor grade biaxially oriented polypropylene (BOPP) with a thickness of 8 µm was obtained from SB Electronics, Inc., Barre, Vermont, USA.

The MLFs were manufactured via microlayer coextrusion by PolymerPlus, LLC, similarly to a process described in an earlier paper[17]. The controls were also extruded by PolymerPlus, LLC. All films were processed with a protective LDPE skin layer that was removed prior to sample preparation for dielectric characterization.

Both MLFs consisted of 33 alternating layers of PC and PVDF with a PC/PVDF volumetric ratio of 70/30. The odd number of 33 layers was chosen so that both outermost layers of the MLF would be the same material, namely PC. The thicknesses of the MLFs and controls varied considerably, from 4 µm to 24 µm. This was considered when choosing samples for dielectric measurements.

The MLF and control samples were dried under vacuum at 110 °C for 24 h and the BOPP samples were dried under vacuum at 55 °C for at least 6 h before
metal coating. Drying was found to be necessary because all the samples, especially the more polar PVDF, absorbed moisture and yielded unreliable dielectric data as a result. After drying, the samples were coated on both sides with a 50 nm thick disk of Au, Ag or Al using physical vapor deposition (EvoVac Deposition System, Angstrom Engineering Inc., Kitchener, Ontario, Canada) to improve electrical contact. The coated electrode areas were 0.0962 cm² for the breakdown testing, 0.0515 cm² for the D-E loop study, and 0.785 cm² for the BDS and leakage current measurements. The samples were stored in a desiccator filled with Drierite until dielectric measurements were performed.

4.2. Differential Scanning Calorimetry

The glass transition temperatures (T_g) of Apec and Calibre were determined on a TA Instruments (New Castle, Delaware, USA) Q2000 differential scanning calorimeter at a scan rate of 10 °C/min. Temperature was scanned from 25 °C to 220 °C, back to 25 °C and then to 220 °C again. T_g's were determined from the second heating curves.

4.3. Broadband Dielectric Spectroscopy (BDS) Measurements

Low voltage BDS measurements were performed with a Novocontrol Concept 80 broadband dielectric spectrometer (Montabaur, Germany). For BDS temperature scan measurements the temperature was programmed to ramp from
-150 °C to 150 °C at a rate of 2 °C/min. A sinusoidal AC voltage of 1 V$_{\text{rms}}$ with the frequency scanning from $10^7$ Hz to 1 Hz within every 15 s was applied across the polymer film sample during the temperature ramping and data was recorded simultaneously. For BDS frequency scan measurements the temperature was held constant and the frequency of the applied AC voltage was scanned from $10^7$ Hz down to $10^{-3}$ Hz. Only Au-coated samples were used for BDS measurements.

### 4.4. Hysteresis Loop Measurements

$D$-$E$ loop measurements were performed using a Premier II ferroelectric tester (Radiant Technologies Inc., Albuquerque, New Mexico, USA). The tester was used to apply a high voltage sinusoidal signal of 10 or 1000 Hz across the sample and record the resulting current which it converted into electric displacement $D$ and plotted against the applied electric field $E$, yielding $D$-$E$ curves (or loops, as they are usually so shaped). Only two sine waves were applied in any one measurement and data from the second wave was used to avoid the transient in the beginning of the first wave. All measurements were performed in silicone oil to control the temperature and to eliminate corona breakdown of air. Measurements were performed at 100, 120, and 150 °C, using a VELP Scientific temperature controller (VELP Scientific, Inc., Bohemia, NY).

In order to get accurate results, stray capacitance due to measurement fixture, cables and other parts was calculated and subtracted from the results.
The stray capacitance was determined by measuring the $D$ of a material of known permittivity, BOPP. Then the stray capacitance of a sample was subtracted from the raw data.

4.5. Leakage Current Measurements

Leakage currents of polymer samples were measured by applying a DC voltage across the sample at a controlled temperature and recording the resulting current for 5 h. Measurements were performed using a Keithley 6517B electrometer in combination with the Novocontrol Concept 80 for temperature control. Leakage current of each sample was measured at a constant electric field of 10, 30 or 40 MV/m, depending on the material, and at temperatures 100, 110, 120, 130, 140, and 150 °C. All the while it was necessary to ensure that electronic conduction current and not current due to ion relaxation is measured. To achieve this, the highest temperature was run first to avoid additional ion relaxation that would happen with going from lower to higher temperatures. Current at each temperature was measured for 5 h and the stabilized current at the end of the 5 h time period was used to calculate the conductivity. All samples for leakage current measurements were Au-coated.

4.6. Dielectric Breakdown Measurements

Due to the large number of samples (about 3000) for this measurement,
special coating masks with grids of holes were made out of a 75 µm thick Kapton® sheet using a laser cutter to ensure that each sample would have exactly the same size and shape of Al coating. Also a special fixture was made out of Teflon with two electrodes to make contact with the samples (Figure 4.1, left panel). The upper electrode is a spring loaded stainless steel rod which ensures that the sample is held down with a constant force. The tip of the stainless steel rod (Figure 4.1, right panel) is cushioned with conductive fluorosilicone (Stockwell Elastomerics, Inc., Philadelphia, Pennsylvania, USA) to prevent damage to the samples. An earlier version of this fixture only had solid copper electrodes resulting in unreliable measurements due to puncturing of the samples, especially at high temperatures.

![Figure 4.1. Teflon fixture for breakdown measurements with a sample under the spring loaded upper electrode (left) and the tip of the upper electrode, covered with a conductive elastomeric cushion (right).](image)

A Quadtech (Marlborough, MA) Guardian 20 kV HiPot tester was used for the breakdown testing. The sample was placed between the electrodes and a
ramping voltage of 500 V/s was applied across the sample until breakdown occurred, which was determined as the point when the current exceeded 5 mA. All breakdown testing was performed using the same temperature control and silicone oil setup as for the $D$-$E$ loop measurements.

RESULTS AND DISCUSSION

4.7. Differential Scanning Calorimetry (DSC) of the PCs

Two types of PCs were used to coextrude with PVDF: A normal bisphenol A PC (BPA-PC), called Calibre in this chapter, with a $T_g$ of 145 °C, and a copolymer PC of BPA and bisphenol TMC[18], called Apec in this chapter, with a $T_g$ of 167 °C. Both MLFs utilized the same PVDF: Solef. The structures of BPA and TMC as repeat units are shown in Figure 4.2.

Figure 4.2. Structures of bisphenol A and bisphenol TMC as repeat units.
The $T_g$s of Apec and Calibre were determined using DSC (see Figures 4.3A and 4.3B).

**Figure 4.3A.** DSC of Apec showing the heat flow vs T and the $T_g$ peak from the second heating curve.
4.8. Broadband Dielectric Spectroscopy (BDS) Study

4.8.1. Calibre (a Normal Bisphenol A Polycarbonate)

The dynamic dielectric properties of the MLFs and the controls (Apec, Calibre and Solef) were studied using BDS, both in temperature and frequency scans. In Figure 4.4A, four transitions can be seen in the dielectric loss spectrum of Calibre in the order of decreasing temperature: \( \alpha \), \( \beta \), \( \gamma_1 \), and \( \gamma \).
Figure 4.4A. $\varepsilon''$ vs. T for Calibre with sub-$T_g$ relaxation peaks ($\beta$, $\gamma_1$, and $\gamma$) and $T_g$ ($\alpha$) identified.
Figure 4.4B. $\varepsilon'_r$ vs. T for Calibre with sub-$T_g$ relaxation peaks ($\beta$, $\gamma_1$ and $\gamma$) and $T_g$ ($\alpha$) identified.
Figure 4.4C. $\varepsilon''$ vs. $f$ for Calibre with sub-$T_g$ relaxation peak $\gamma$, $T_g (\alpha)$, and an ion peak identified.
Figure 4.4D. $\varepsilon'_r$ vs. $f$ for Calibre with sub-$T_g$ relaxation peak $\gamma$ and $T_g$ ($\alpha$) identified.

The molecular origins of the $\alpha$-transition in BPA-PC result from segmental cooperative movements of the polymer chain as the temperature approaches $T_g$.[19] The $\beta$ relaxation results from 180° flips of the phenyl groups when the adjacent carbonyl groups interchange their conformations between *cis-trans* and *trans-trans*.[20] The presence of the $\gamma_1$-transition depends on the thermal history of the sample. Fontanella et al.[21] noticed that the $\gamma_1$-peak appears as a shoulder to the $\gamma$-transition if the sample has been heated even slightly above room temperature before making the dielectric measurement. In our case, a BDS
frequency-scan at high temperatures was run before the temperature-scan, and this explains the appearance of the $\gamma_1$-peak.

The $\gamma$-transition is considered to consist of several relaxation peaks, and is related to the motion of both the carbonate group and the phenyl rings.[22] According to Jones,[23] data from solid-state NMR studies indicate that the carbonate group exchanges its *cis-trans* conformation with a *trans-trans* conformation of a neighboring carbonate group, allowing the conformation to diffuse along the polymer chain.[19]

### 4.8.2. Apec (a BPA and Bisphenol TMC Copolymer)

Apec, a copolymer of bisphenol A and bisphenol trimethyl cyclohexane (TMC) has a $T_g$ about 20 °C higher than that of Calibre. Apec exhibits the same kind of sub-$T_g$ transitions as Calibre, including the $\gamma$-transition (see Figure 4.5A) but it lacks the $\gamma_1$-transition. Because of its higher $T_g$, there is no sharp increase of $\varepsilon_r''$ at 150 °C.
Figure 4.5A. $\varepsilon''_r$ vs. $T$ for Apec with the $\gamma$ and $\beta$ relaxation peaks identified.
Figure 4.5B. $\varepsilon'_r$ vs. $T$ for Apec with the $\gamma$ and $\beta$ relaxation peaks identified.
Figure 4.5C. $\varepsilon''$ vs. f for Apec with the $\gamma$ and $\beta$ relaxation peaks identified. A slight ion peak can be noticed at the lowest frequencies in the 150 °C curve.
Figure 4.5D. $\varepsilon'_r$ vs. f for Apec with the $\gamma$ and $\beta$ relaxation peaks identified.

4.8.3. Solef

About 50% of PVDF is amorphous and the rest is crystalline,[14] which may often exhibit a mixture of $\alpha$, $\beta$, $\gamma$, and $\delta$ phases.[24] Four relaxation peaks can be seen in the dielectric loss spectrum of melt-crystallized Solef (mostly $\alpha$ phase in crystals) in Figure 4.6A. At high temperatures, free volume between the polymer chains increases allowing impurity ions to move more freely, which gives rise to an increased ionic loss[25]. The $\alpha_c$ relaxation arises from the $\alpha$-crystalline phase of the PVDF,[26] where the slightly tilted CF$_2$ dipoles switch back and forth along the polymer chain axis.[27] The $T_g$ (or the $\alpha$ transition) results from
segmental cooperative motion in the amorphous phase.[28] The amorphous dipoles begin to move at a relatively low field in the BDS measurement (about 0.1 MV/m). This field is not high enough to switch the dipoles in the crystalline phase of PVDF: this would require a field of about 70 MV/m for the $\beta$ dipoles.[29] The $\beta$-transition arises from the localized crank-shaft molecular motions in the amorphous phase.[30]

Above 75 °C in Figure 4.6A the $\varepsilon''$ curve rises steeply. The phenomenon of the rising $\varepsilon''$ in the temperature scan can be better observed in the frequency scan for $\varepsilon''$ in Figure 4.6C where at frequencies below 100 Hz the $\varepsilon''$ curve for 150 °C has a slope of about -1 which is indicative of electronic and ionic conduction loss.[31] The electronic conduction loss of PVDF was calculated from the relation: [32]

$$\varepsilon'' = \frac{\sigma'}{\varepsilon_0 \omega},$$

where $\sigma'$ is the real part of the conductivity, $\varepsilon_0$ is the vacuum permittivity, and $\omega$ is the angular frequency ($\omega=2\pi f$). The conductivity was taken from leakage current data of Solef at 150 °C (a value of $6\times10^{-12}$ S/m). The calculated electronic loss curve (magenta line in Figure 4.6C) was overlaid with the frequency scan plot. As can be seen from Figure 4.6C, the dielectric losses from BDS are about 1 order of magnitude higher than those of the electronic loss curve. This indicates that most of the dielectric loss in PVDF Solef at frequencies below 100 Hz result from ionic conduction and not electronic conduction.
**Figure 4.6A.** $\varepsilon''$ vs. $T$ for Solef with $\beta$, $T_g$, $\alpha_c$, and fast ion relaxation peaks identified.
Figure 4.6B. \( \varepsilon'_r \) vs. vs. \( T \) for Solef with \( \beta \), \( T_g \), \( \alpha_c \), and fast ion relaxation peaks identified.
Figure 4.6C. $\varepsilon''$ vs. f for Solef, showing the $\alpha_c$ relaxation peak and the loss curve with a slope of -1 characteristic of ionic conduction. The electronic conduction loss (magenta curve) is calculated from leakage current measurements at 150 °C.
Figure 4.6D. $\varepsilon'_{\alpha}$ vs. $f$ for Solef, showing the $\alpha_c$ relaxation peak and the increase in permittivity due to impurity ion migration.

4.8.4. BDS of MLFs

Figure 4.7A shows the dielectric loss spectrum of $\varepsilon''$ vs. $T$ for the Calibre/Solef 70/30 33L film with all peaks identified from the controls. The shoulder present in the BDS temperature-scan spectra of both Calibre/Solef and Apec/Solef MLFs at 115 °C of the 1 Hz curve in Figures 4.7A, 4.7B, 4.8A, and 4.8B is attributed to ionic conduction of the PVDF. This ionic conduction can be more clearly seen in neat PVDF in Figure 4.6A for the 1 Hz curve, beginning at 75 °C. This ion peak is also visible in the $\varepsilon''$ vs. $f$ curves (Figures 4.7C and 4.8C)
labeled as “fast ions” because there is discernible another ion peak towards lower frequency, resulting from even slower ions, labeled as “slow ions” in Figures 4.7C and 4.8C. For the origins of ionic species in PVDF, they most likely come from the synthesis of the PVDF resin using emulsion or suspension polymerization with added surfactants.[33]

![Diagram of Calibre/Solef](image)

**Figure 4.7A.** $\varepsilon''$ vs. $T$ for Calibre/Solef with various relaxation peaks identified.

The only significant difference that can be seen between the Apec/Solef and Calibre/Solef MLFs is that Calibre/Solef has a higher loss (by a factor of 2 or 3) at the high temperature end (>100 °C) of the temperature-scan at low frequencies (compare Figures 4.7A and 4.8A). This is because of an increased
ionic conduction in Calibre due to an increased free volume as the temperature is close to the $T_g$.[25]

**Figure 4.7B.** $\varepsilon'_r$ vs. $T$ for Calibre/Solef with various relaxation peaks identified.
Figure 4.7C. $\varepsilon''$ vs. f for Calibre/Solef with various relaxation peaks identified.
Figure 4.7D. $\varepsilon_r'$ vs. f for Calibre/Solef with various relaxation peaks identified.
Figure 4.8A. $\varepsilon''$ vs. $T$ for Apec/Solef with various relaxation peaks identified.
Figure 4.8B. $\varepsilon'$ vs. $T$ for Apec/Solef with various relaxation peaks identified.
Figure 4.8C. $\varepsilon''$ vs. $f$ for Apec/Solef with various relaxation peaks identified.
4.9. D-E Loops

4.9.1 Choice of Electrode Material

It is important to choose the right electrode material when coating samples for dielectric testing. Three metals were tested for use as electrodes: Ag, Au and Al. One has to keep in mind that D-E loop measurements were performed under physically aggressive conditions of high temperatures, up to 150 °C, and a high electric field of 200 MV/m or higher. These conditions are conducive to electrochemical reactions and corrosion of the metal electrodes.
First, Ag was used as the electrode material. The \( D-E \) loop\(^1 \) obtained using 50 nm Ag electrodes coated on the Apec PC is shown in Figure 4.9F, measured at 1 Hz and 150 °C with the electric field ramped up to 200 MV/m. For this part of the study, \( D-E \) loops at 1 Hz, as opposed to the conventional 10 Hz, were measured to elucidate the loss mechanisms which tend to become magnified at lower frequencies. The loop in Figure 4.9F is quite broad and is spiraling down which is quite peculiar. \( D-E \) loops of samples with gold and aluminum coated electrodes (Figures 4.9B and 4.9D) that were measured exactly under the same conditions, do not exhibit down-spiraling. An earlier study by Yang et al.[27] could shed some light on this spiraling phenomenon. They observed that the DC conductivity of Ag coated PVDF is about 30 times higher than that of Al coated PVDF at 100 °C. Thermally stimulated depolarization current (TSCD) experiments with Ag- and Al-coated PVDF showed that Ag injects a significant amount of homocharges (i.e., injected real charges with the same polarity as the electrode) into the dielectric polymer. Yang et al. mentioned that the injected homocharges could also induce electrochemical reactions, producing HF from PVDF at high temperatures and high electric fields, which corroded the Ag electrodes.[27] However, we here observed downward spiraling of \( D-E \) loops of neat Ag-coated PC (Apec) samples. Since HF could not be released from PC, there must be additional processes that give rise to the spiraling of the \( D-E \) loop. A possible explanation could be electrochemical reactions which occur on the Ag electrodes, causing additional current in the testing circuit which could explain

\(^1\) The reader is encouraged to refer to section 3.2 of this dissertation for an explanation on how to interpret \( D-E \) loop data.
the spiraling of the $D$-$E$ loop, since there could be irreversible reactions which only occur during one half of the $D$-$E$ loop (e.g., negative only) but not the other. This would result in the spiraling with the second loop finishing lower than the origin point.

Second, Au was tested as an electrode material. While the $D$-$E$ loops with Ag electrodes were extremely broad, Au electrodes also produced a broadening compared to Al electrodes, comparing Figures 4.9B and 4.9D, but this time the broadening was symmetrical about the x-axis, perhaps pointing to a loss from ionic conduction.[34] However, that would not explain why the Au-coated sample exhibits more ionic conduction loss than the Al-coated sample because both had the same PC Apec. Another explanation could be electrochemical reactions (which could also produce ions). Au, for example, can form an oxide under aqueous conditions at an electrode potential of 1.36 V vs RHE.[35] We need to keep in mind that if a monolayer of Au oxide ($\text{Au}_2\text{O}_3$) was produced on the Au electrode, this would result in a $D$ value of about 4000 mC/m$^2$,[35] which is about two orders of magnitude higher than the polarizations obtained in our $D$-$E$ loops. This means that even a small fraction of the redox reaction in the sample or on the metal electrode could produce a large change in the $D$-$E$ loop. A related phenomenon was noted by Yang et al.[27] who ran TSDC experiments with Al and Au electrodes, and noticed the disappearance of an alleged ion depolarization peak when Au electrodes were used.
Figure 4.9. Effect of coated electrode material on the $D$-$E$ hysteresis loops, measured at 150 °C using the Apec film.
From the above results, Al electrodes yielded $D$-$E$ loops with the lowest losses (Figure 4.9B) and Al thus seems to be the most practical for use in polymer film capacitors primarily because of its low price and a reasonably good corrosion resistance under harsh high temperature and high electric field conditions.

In conclusion, the effects that different electrode materials have on ion and charge injection, as well as on conductivity of polymer films, definitely invite further investigation.

### 4.9.2. $D$-$E$ Loops of MLFs and Controls

$D$-$E$ hysteresis loops were measured to determine the dielectric properties of MLFs and controls at high electric fields (up to 400 MV/m) and high temperatures. Only Al electrodes were used to obtain the $D$-$E$ loops discussed in this section. The advantage of the MLFs is their higher energy density comparing with pure PC and much lower hysteresis loop loss, comparing with pure PVDF. At 120 °C and 1000 Hz, the Apec/Solef MLF has a 21% higher discharged energy density than pure Apec, as calculated from the $D$-$E$ loops in Figures 4.10B and 4.17C. This increase in energy density is due to the dipolar polarization of amorphous PVDF dipoles.

The $D$-$E$ loops of Calibre/Solef exhibit from 50% to 100% more loss than those of Apec/Solef at each of the temperatures and frequencies measured (Figures 4.12 and 4.13). Let us look more closely at the $D$-$E$ loops of Apec/Solef
and Calibre/Solef at 150 °C and 10 Hz (Figures 4.12E and 4.12F) because these are the conditions under which the loss mechanisms are most clearly observed. The loop for Apec/Solef is narrower and more symmetrical about the x-axis than the loop for Calibre/Solef whose upper half is very much up-shifted. This indicates that most of the loop loss for Calibre/Solef comes from electronic conduction. That is because as the temperature gets closer to the T_g, the PC becomes more conductive. On a detailed observation, one can also notice that the lower halves of the Apec/Solef loops are more down-shifted at each temperature compared to the Calibre/Solef loops. This indicates that there is more ionic conduction loss for the Apec/Solef films. Figures 4.10C and 4.11C give an answer: pure Apec also exhibits more ionic conduction loss than pure Calibre and this same ionic conduction loss in PC is carried over to the MLFs.

Comparing the 10 Hz and 1000 Hz loops at 150 °C (Figures 4.12 and 4.13), the 1000 Hz loops are very narrow because neither ionic nor electronic conduction contribute much to the loop loss at 1000 Hz because it takes time for ions or electrons to flow and build up charge.

It is interesting to note, looking at the D-E loops of Apec and Calibre (Figures 4.10 and 4.11), that these two PCs, despite their different T_g's, have quite similar loop losses at 120 °C and 150 °C. It is only when they are combined with PVDF in MLFs that the loss for the Calibre-containing MLF increases more than that of the Apec-containing MLF (Figures 4.12E and 4.12F). This is because at temperatures close to the T_g of Calibre, PC can no longer act as a blocking layer to the large amount of charge carriers in PVDF, and begins to allow the
injection and passage of these charge carriers. More specifically, as temperature approaches the $T_g$, the free volume in Calibre increases, making it more conductive to impurity ions in PVDF.[25] Also, because the interfacial polarization[15] (i.e., the accumulation of ions and electrons/holes at the PC/PVDF interfaces due to the applied electric field), which blocks passage of charge carriers between layers, ceases, the PC/PVDF interface can become more conductive to electrons and holes traveling from PVDF into PC.

Another thing worth noticing is that for pure Solef at 10 Hz, the $D-E$ loop losses almost do not change between 120 and 150 °C (see Figure 4.14). This is because of the ferroelectric switching of crystalline dipoles. At 1000 Hz, ferroelectric switching cannot catch up with the field frequency. A relatively linear behavior is observed at both 120 and 150 °C. Also, the $D-E$ loops for Solef were measured to a lower field of 125 °C because of its lower breakdown strength.

In conclusion, the Apec/Solef MLF is better than the Calibre/Solef MLF at high temperatures because of the lower ionic and electronic conduction of Apec due to its higher $T_g$.

When comparing MLFs with BOPP (see Figure 4.15), it is apparent that BOPP still has the lowest loop losses, about 0.7% at 120 °C and 1000 Hz. We conclude that $D-E$ loop measurements cannot explain why BOPP becomes unusable in capacitors above 105 °C.[6] This is because the duration of $D-E$ loop measurements is too short, only from 2 to 200 ms. This does not give the films enough time to develop failure modes that make them unusable at high
temperatures. Therefore, another type of experiment is needed, either longer in duration (lifetime study) or at more extreme conditions (breakdown testing).

Initially the D-E loop measurements on the MLFs were performed up to a field of 400 MV/m (see Figures 4.16 and 4.17), just like those for the PC controls. However, as can be seen from Figure 4.16, these loops often exhibited an initial transient that shifted the loops completely up relative to the x-axis. Also, some downward spiraling occurred. These phenomena, that only seemed to occur in MLFs at field strengths above about 250 MV/m, tended to overshadow some effects that were visible at a lower field of 200 MV/m. Hence data at 200 MV/m was discussed first.

At 400 MV/m, which is a relatively high field, there may occur a charge injection from the negative electrode into the first layer (PC) of the MLF because of the higher local field in the PC layer (because of its low k). To understand why the local field in the PC layers of our MLFs is high, let us look at the following equations giving the field strength in each individual layer of an MLF:

\[ E_{PC} = \frac{\varepsilon_{PVDF}}{\varepsilon_{PC} d_{PVDF} + \varepsilon_{PVDF} d_{PC}} V \]  \hspace{1cm} (4.1)

\[ E_{PVDF} = \frac{\varepsilon_{PC}}{\varepsilon_{PC} d_{PVDF} + \varepsilon_{PVDF} d_{PC}} V \]  \hspace{1cm} (4.2)

where \( d \) is the sum of thicknesses of all layers of either PC or PVDF in a sample and \( V \) is the voltage across the sample.
For 70% PC and 30% PVDF these equations can be approximated to yield \( E_{PC} = E_{TOTAL} \times 1.3 \) and \( E_{PVDF} = E_{TOTAL} \times \frac{1}{3} \). From here we see that the higher the k (or, permittivity), the lower the field inside the material. Therefore if 400 MV/m is applied across a sample, the field in the PC layers would be \( E = 400 \times 1.3 = 520 \) MV/m. Such high fields can produce field emission of electrons and thus charge injection from the coated metal electrodes into the polymer film.[36] A possible charge injection could be seen in the D-E loops in Figures 4.16E and 4.16F, where the beginning of the loop suddenly curves upwards at about 250 MV/m. In addition to this, electrochemical reactions are possible which cause down-spiraling of the loops, such as in Figure 4.16F. A possible solution to the field emission problem would be to make the first layer, which is in contact with the metal electrode, out of a high k material to produce (according to equations (4.1) and (4.2)) a low field near the metal which would not induce field emission of electrons. PVDF would be one such material but unfortunately due to its softness, it can approach too close to the surface of the electrode, making it susceptible to electrochemical reactions. A better alternative is \( \text{Al}_2\text{O}_3 \) that also has a high k but should not be susceptible to electrochemical reactions.
Figure 4.10. D-E loops for Apec at different temperatures and frequencies.
Figure 4.11. $D$-$E$ loops for Calibre at different temperatures and frequencies.
Figure 4.12. D-E loops for the Apec/Solef and Calibre/Solef MLF at different temperatures and frequencies, measured up to 200 MV/m at 10 Hz.
Figure 4.13. $D$-$E$ loops for the Apec/Solef and Calibre/Solef MLF at different temperatures and frequencies, measured up to 200 MV/m at 1000 Hz.
Figure 4.14. $D$-$E$ loops for Solef at different temperatures and frequencies. Note that the scales on the axes here are different from the previous $D$-$E$ loop plots.
Figure 4.15. $D$-$E$ loops for BOPP at different temperatures and poling frequencies.
Figure 4.16. D-E loops for the Apec/Solef and Calibre/Solef MLF at different temperatures and frequencies, measured up to 400 MV/m at 10 Hz.
Figure 4.17. $D$-$E$ loops for the Apec/Solef and Calibre/Solef MLF at different temperatures and frequencies, measured up to 400 MV/m at 1000 Hz.
4.10. Breakdown Study

Since BDS and $D-E$ loop studies cannot effectively predict extreme dielectric properties, a Weibull breakdown study was carried out. A total of about 2500 single breakdowns were analyzed using Weibull statistics – a method commonly used in failure analysis and for dielectric breakdown studies.[37, 38] Data points are plotted as probability of breakdown (or, Weibull percentile) vs electric field (Figure 4.18). For a single breakdown mechanism such plotting of data points yields straight lines. The higher the slope $\beta$ of the lines, the narrower the range of electric field values in which all samples break down. A narrow range, and thus, a high slope, is desired for producing dielectric films with good quality and consistent breakdown properties.

The breakdown strengths of BOPP, the MLFs (Apec/Solef and Calibre/Solef), and the controls (Apec, Calibre, and Solef) were tested at various temperatures, and the results are shown in Figure 4.19. The breakdown strengths reported are given as the characteristic field strength, i.e. the electric field strength with a 63.2% probability of failure (see Figure 4.18).

Figure 4.19C shows that Apec/Solef has a breakdown strength about 150 MV/m (ca 25%) higher than Calibre/Solef despite the fact that the breakdown strength of Apec is only about 90 MV/m higher than that of Calibre. To understand this discrepancy, let us look at the structure of the MLFs. The multilayer films consist of alternating layers of high $k$ (e.g., PVDF) and low conductivity (e.g., PC) materials. The low conductivity material acts as a so-
called “blocking electrode”. MLFs show a higher breakdown strength than the individual components making up the MLFs, which has been reported previously.\[12, 37, 39\] From our leakage current studies, we found that Solef is about 3 orders of magnitude more electronically conductive than the PC films. Also, from BDS data (Figure 4.6C and 4.6D), we can see a large increase in loss at low frequencies due to ionic conduction, meaning there is a relatively high concentration of mobile ions in PVDF. PVDF has much more charge carriers than PC. The reason why the Apec/Solef MLF performs so much better than the Calibre/Solef MLF in breakdown tests is because of interfacial polarization of the above mentioned charge carriers. Apec, because of its higher \( T_g \), does not allow the protective interfacial polarization in PVDF to dissipate, whereas the lower \( T_g \) Calibre allows the charge carriers at the interface to pass through, effectively removing the protective interfacial charged layers and thus letting the breakdown spread through the layers of the MLF.

Most interestingly Calibre/Solef has a lower breakdown strength and lower Weibull slope \( \beta \) (Figures 4.19C 4.19D) than Apec/Solef throughout the entire temperature range from 25 °C to 150 °C, so even when far below its \( T_g \), Calibre/Solef still performs much worse than Apec/Solef. The high temperature breakdown strength difference could be attributed to the difference in \( T_g \) but the lower temperature difference in breakdown strength is harder to explain.

As for the Weibull slopes (Figure 4.19D), Apec/Solef has the highest slope and Calibre/Solef has one of the lowest among all materials tested. But surprisingly, Apec has a much lower Weibull slope than Calibre. In order to
understand these results, we have to keep in mind that a Weibull slope is an indicator of the quality of the film, i.e. it depends not so much on the intrinsic properties of the material but on the way the film was manufactured. Extrinsic defects, such as pinholes could cause Apec to exhibit a low Weibull slope.

BOPP seemed to be the best material at room temperature (850 MV/m) but it only lasted up to 120 °C (575 MV/m) and dropped off dramatically above that, whereas Apec/Solef was about 75 MV/m higher in breakdown strength at 120 °C and could go as high as 150 °C still performing reasonably. Above 120 °C BOPP became mechanically unstable and began to shrink. The breakdown strength of BOPP has been studied extensively by Ho et al. [9] [6], who found that the breakdown strength of BOPP was 712 MV/m at room temperature and decreased to 640 MV/m at 100 °C which is in good agreement with our results.

In order to shed light on why the performance of BOPP declines at higher temperatures, BOPP samples were annealed at different temperatures for a period 6 h before performing breakdown testing at room temperature. It was found that the breakdown strength of BOPP decreases with higher annealing temperatures (Figure 4.20). We suspect extrinsic defects may be developing in BOPP at higher temperatures as a result of its history of biaxial stretching. This could be a reason why BOPP performs poorly at higher temperatures.

The Weibull slope depends more on the quality of the film and the existence of extrinsic defects (such as mechanical damage). Our first approach in breakdown testing was to use a solid copper upper electrode in the breakdown fixture. The electrode tip would gimbal to be perfectly parallel with the lower
electrode not to puncture the sample. This approach was unsuccessful because due to its small size (diameter 1.9 mm) the tip of the upper electrode was not always parallel with the lower one and thus pinched the sample. This made the Weibull slope $\beta$ inconsistent as can be seen in Figure 4.21B, comparing with data obtained with a soft conductive elastomer tip (Figure 4.21A) which was ultimately used for this breakdown study.

In conclusion, the Apec/Solef MLF is the best performing material to use, especially in applications where high temperatures are required (above 120 °C), where BOPP cannot perform at all.

![Weibull plots of PC Apec showing the individual data points and reference lines at different temperatures.](image)

**Figure 4.18.** Weibull plots of PC Apec showing the individual data points and reference lines at different temperatures.
Figure 4.19. Characteristic breakdown strength of BOPP (A) and of the multilayer films and controls (C), and Weibull slopes of BOPP (B) and the multilayer films and controls (D).
Figure 4.20. Room temperature Weibull breakdown strength of BOPP as a function of annealing temperature (°C).

Figure 4.21. Weibull slope $\beta$ as a function of temperature for the MLFs and controls, as measured with the soft-tip electrode (A) and the hard, non-cushioned copper electrode (B).
4.11. Leakage Current Study

Leakage current measurements were performed at various temperatures up to 150 °C to learn about the electronic conductivity of the MLFs, and the controls (Apec, Calibre, Solef). A plot of conductivity vs. temperature is shown in Figure 4.22B.

In our initial leakage current measurements we erroneously concluded that there is a large electronic charge injection from PVDF into PC in the MLFs. The initial measurements were conducted at electric fields from 5 to 80 MV/m and at temperatures 100, 110, 120, 130, 140, and 150 °C. For each sample the measurement began at the lowest field of 5 MV/m, running from 150 °C down to 100 °C, applying voltage at each temperature for 30 minutes. The stabilized current at the end of each 30 min time period was used to calculate the conductivity. It was initially found that MLFs exhibit about an order of magnitude higher conductivity in leakage current measurements than is theoretically predicted from the conductivities of the individual component control films (Figure 4.22A). We then found a much better explanation to this phenomenon. First of all, the leakage current measurements were repeated but instead of measuring the current for 30 minutes, it was now measured for 5 hours to allow any ionic conduction to decay to a minimum. In retrospect, the initial measurements with 30 min per temperature (Figure 4.22A) were not off by much because several fields (each running through all the 6 temperatures) were measured before
reaching the field used to calculate the conductivity here and this resulted in the sample having been poled for several hours before the measurement of interest.

The conductivities based on the new, 5 h measurements are shown in Figure 4.22B. According to this, Solef was about 1000 times more electronically conductive than Apec. PVDF is so conductive for a few reasons. Ionic impurities are easily introduced through surfactants during the manufacture process.[33] Its high ionic conductivity is evident from earlier BDS measurements. In Figure 4.23A the ionic conduction loss of PVDF is compared with the electronic conduction loss\(^2\), represented by the magenta line. The ionic conduction in PVDF is clearly very high, esp. at the low frequencies. For comparison, Figure 4.23B shows the same plot for Apec with a 100,000 times lower ionic conduction loss at the low frequency end. Also, PVDF is a polar polymer and easily attracts polar impurities, such as ions and water. Finally, PVDF has a low \(T_g\), and the high mobility of amorphous PVDF chains enhances electronic conductivity via the hopping mechanism.

\(^2\) The electronic conduction loss was calculated based on conductivity from leakage current measurements.
Figure 4.22. Bulk conductivities as a function of temperature measured by leakage current study at 30 MV/m for various films, comparing 30 min and 5 h measurements.

Figure 4.23. Dielectric loss of Solef (A) and Apec (B) with loss from electronic conduction (as calculated from leakage current measurements) plotted in magenta.

Now to explain why leakage current measurements of MLFs could easily lead to incorrect interpretations. The leakage current measurements were conducted by applying a DC voltage for 5 hours across to the sample at a constant temperature and only one field. The highest temperature (150 °C) was
measured first, then decreasing the temperature by 10 degree decrements. For the first (150 °C) measurement of PVDF, a large current drop can be seen during the first 20 minutes (Figure 4.24B). This is attributed to the ionic current decaying as the ions reach an equilibrium in the sample.

**Figure 4.24.** Leakage current as a function of time at different temperatures.

When Apec is multilayered with Solef, the system behaves like two series resistors with the PC being 1000 times more resistive than PVDF. When voltage is applied across such a sample, most of the voltage drop occurs on the PC (99.9%) and PVDF will only experience about 1/1000 of the total voltage drop. This means the electric field in the PVDF is very low, hundreds of times lower.
than when measuring a pure PVDF control. Since the ions in PVDF experience a very low field, it takes them much longer to reach equilibrium within each PVDF layer and thus the measured current, even at 5 h, will mostly represent the ionic, not electronic conduction (Figure 4.24C) but we initially interpreted this result as the MLFs being 10 times more conductive than a series combination of resistors of PC and PVDF. Calculations are currently underway to determine how long to apply a DC voltage across an MLF to reach a steady state to measure the actual electronic conductivity.

BOPP was the second most conductive (Figure 4.24A). The values reported here agree well with the results of Ho et al. who tested BOPP extensively.[40] From the leakage current measurements, we also learned that BOPP does not withstand high temperatures and high fields for a long period of time which is required to run leakage current measurements. This is another hint that a lifetime study is needed to test the long term high temperature performance of BOPP.

Calibre is about 5 times more conductive than Apec at 100 ºC and about 10 times more conductive at 150 ºC (Figure 4.24B). Calibre becomes more conductive as it approaches its $T_g$ of 145 ºC. The conductivity curve of Apec also bends slightly upwards as the temperature approaches its $T_g$ of 167 ºC.

Calibre/Solef is still about 10 to 20 times more conductive than Apec/Solef (Figures 4.22B) and these results are not affected by the above findings about ionic conduction because both films contain the same volume fraction of the same PVDF and the difference can only be attributed to the polycarbonate.
Calibre/Solef MLF is more conductive than the Apec/Solef MLF because Calibre, with a lower $T_g$ is more susceptible to charge injection from Solef, leading to reduced interfacial charge densities at the PC/PVDF interfaces and performing as a worse blocking electrode.

Finally, we note an inverse relation between conductivity and breakdown strength of the films studied, based on Figures 4.19C and 4.22B. This is not surprising because breakdown processes have been know to be initiated by conduction.[36]

**CONCLUSIONS**

It was found that PVDF injects charge carriers into PC when in contact with it, and the charge carrier injection happens more easily if the PC is closer to its $T_g$. That explains why the MLF Apec/Solef performs better in breakdown tests and has lower conductivity than Calibre/Solef: the higher $T_g$ of Apec helps it maintain the interfacial polarization at its interfaces with PVDF.

Leakage current measurements indicate that PVDF Solef is about 1000 times more electronically conductive than PC Apec. In an MLF this results in a very low field in the PVDF layers during leakage current measurements. From BDS and leakage current data it was found that PVDF contains ions that are responsible for most of its dielectric loss at low frequencies. All this makes it difficult to measure the electronic conductivity of MLFs because in this low field it takes a very long time for the ionic current in PVDF to decay.
Although they exhibit lossier D-E loops than BOPP at lower temperatures, MLFs perform better than BOPP in breakdown testing at temperature above 120 °C because of interfacial polarization. Regarding the high temperature performance of BOPP, D-E loop measurements are too short in test time and cannot clarify how the performance of BOPP degrades at high temperatures over a long time. A lifetime study is needed. An annealing experiment already pointed to the reason for the poor high temperature performance of BOPP: a possible development of extrinsic defects at high temperature due to its history of biaxial stretching.

It was also found that Ag and Au electrodes seem to exhibit electrochemical reactions and are susceptible to corrosion at high temperatures and high electric fields, especially in D-E loop measurements, resulting in broadened and spiraling D-E loops. Al electrodes were found to yield the most consistent D-E loops and we thus recommend using Al for dielectric measurements.

Above a field of 250 MV/m a possible field emission of electrons from the metal electrode into the MLF was observed, causing upshift of D-E loops. It is thought that this field emission is caused by the high field present in the PC layer adjacent to the metal electrode. We propose replacing the low k PC layer with a high k material such as Al₂O₃ to reduce the field and prevent field emission and its related polymer degradation and increased loss.
REFERENCES


CHAPTER 5

Enhancing Electrical Energy Storage Using Polar Polyimides With Nitrile Groups Directly Attached to the Main Chain

ABSTRACT

A set of 12 new polyimides (PIs) with one or three polar CN dipoles directly attached to the aromatic diamine part were synthesized and their electric energy storage properties were studied using broadband dielectric spectroscopy (BDS) and electric displacement–electric field (D–E) loop measurements to determine their potential for high temperature film capacitors for aerospace applications. It was found that adding highly polar nitrile groups to the PI structure increased permittivity and thus electrical energy storage, especially at high temperatures, and 3 CN dipoles were better than 1 CN dipole. Below the glass transition temperature ($T_g$), a weak $\gamma$ transition was observed around $-100\,^\circ\text{C}$ and a broad $\beta$ transition was observed between 100 and 150 $^\circ\text{C}$. It was the $\beta$ (i.e., precursor dipolar motion before long-range segmental motion, or glass transition), rather than the $\gamma$ sub-$T_g$ transition that substantially increased the

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permittivity of PIs. From the BDS results on PIs having 3 nitrile groups, the enhancement in permittivity from permanent dipoles decreased with dianhydride in the order of pyromellitic dianhydride (PMDA) > 4,4′-oxydiphthalic dianhydride (OPDA) > 1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA) > 4,4′-benzophenonetetracarboxylic dianhydride (BTDA). Meanwhile, the increase in permittivity also decreased in the order of para–para, meta–para, and meta–meta linkage in the diamine, suggesting that the para–para linkage favored easier dipole rotation than the meta–meta linkage. From the D–E loop study, the PIs with a combination of PMDA dianhydride and a para–para linkage exhibited the highest discharged energy density and a reasonably low loss.

INTRODUCTION

High dielectric constant (>5–10), high temperature (>150 °C), and low loss polymers are attractive dielectric materials for a variety of practical applications\(^1,2\) such as film capacitors for power-conditioning,\(^3–5\) power electronics in hybrid electric vehicles,\(^6–8\) pulsed power,\(^9–11\) and gate dielectrics for field-effect transistors.\(^12,13\) There have been several strategies to achieve this goal. First, a significant amount of research effort has been dedicated to converting high dielectric constant ferroelectric polymers such as poly(vinylidene fluoride) (PVDF) and its random copolymers into more or less linear dielectrics.\(^14,15\) It is observed that decreasing the ferroelectric domain size to the nanoscale (i.e., nanodomains) by repeat-unit crystal isomorphism can effectively achieve the so-
called relaxor ferroelectric behavior showing a narrow hysteresis loop.\textsuperscript{15} As a consequence, a high dielectric constant in the range of 30–70 can be obtained with reasonably low dielectric loss. However, repeat-unit crystal isomorphism introduces defects in the crystal lattice and tends to decrease the melting temperature ($T_m$). For example, relaxor ferroelectric P(VDF-co-trifluoroethylene-co-1,1-chlorofluoroethylene) [P(VDF-TrFE-CFE)] and P(VDF-co-trifluoroethylene-co-chlorotrifluoroethylene) [P(VDF-TrFE-CTEF)] random terpolymers have a $T_m$ around 125 °C, compared with the $T_m$s of PVDF (175 °C) and P(VDF-TrFE) (ca. 155 °C).\textsuperscript{15–18} Furthermore, nanosized ferroelectric domains decrease the ferroelectric-to-paraelectric (\textit{i.e.}, Curie) transition temperature ($T_C$) to around room temperature for both random terpolymers. Above room temperature, the terpolymers are in the paraelectric phase, where random dipoles highly interact with one another without any existence of ferroelectric domains. In addition to the decreased dipolar polarization for the high temperature paraelectric phase of P(VDF-TrFE), high crystalline and amorphous dipole mobilities promote ionic and electronic mobility in the material, resulting in high dielectric losses.\textsuperscript{15,19} Therefore, the challenge lies in the effort of achieving high temperature relaxor ferroelectric crystalline polymers.

The second strategy is to add permanent dipoles into a high $T_g$ amorphous polymer matrix while avoiding the formation of ferroelectric domains. This is similar to dipolar glasses in ceramic materials,\textsuperscript{20,21} and analogous to spin glasses in magnetic materials.\textsuperscript{22,23} The idea is to utilize the free volume in high $T_g$ polymers to allow relatively free rotation of individual dipoles (\textit{i.e.}, sub-$T_g$
transitions\(^{24}\) in order to enhance the dielectric constant while keeping dielectric loss low. Early work utilized nitrile-containing styrenic and acrylic amorphous polymers to achieve relatively high dielectric constant.\(^{25,26}\) For example, poly(4-vinylbenzylcyanide) was reported to exhibit a dielectric constant as high as 7.0 at 100 kHz. Recently, polar \(\Phi-\text{F}\)^{27} and nitrile\(^{28}\) groups were added into bisphenol A polycarbonate (PC) in order to increase its dielectric constant \((\varepsilon_r = 2.95)\). For example, a fluorinated tetraaryl bisphenol A PC, DiF \(p\)-TABPA-PC, exhibited a dielectric constant of 3.3,\(^{27}\) and a nitrile-modified bisphenol A PC exhibited a dielectric constant of 4.0 at room temperature.\(^{28}\)

Stimulated by the above promising work, we here focus on high performance polyimides (PIs), which are attractive materials for use in highly aggressive environments because of their high \(T_g\), mechanical toughness, and resistance to solvents, radiation, heat and oxidation.\(^{29}\) These properties make PI films highly suitable for use in high temperature applications such as aerospace power conditioning, electronics industry, and electrical insulation materials. Previously, Kakimoto \textit{et al.} reported that attaching nitrile pendants into PIs would enhance their dielectric constants,\(^{30}\) and two PIs from an unsymmetrical diamine with nitrile groups showed poor solubility in aprotic solvents and only became soluble after the nitrile groups were hydrolyzed.\(^{31}\) Their dielectric properties, however, were not reported. Hybrid films based on nitrile-containing PIs/inorganic particles (pyrite ash, barium and titanium oxides) were prepared and their nano-actuation was investigated.\(^{32,33}\) PIs containing one and two nitrile groups per repeat unit were synthesized and their piezoelectric behavior was analyzed. The
polymer containing two nitrile groups per repeat unit showed higher remnant polarization than the ones containing only one nitrile group per repeat unit due to its increase in polarity. However, their values were low as compared with commercial piezoelectric polymers such as PVDF.34

In this work, highly polar nitrile groups are directly attached to the aromatic diamine part of various PI structures. In total, 12 new PIs, containing 1 or 3 CN dipoles, are synthesized. Their dielectric properties and loss mechanisms are studied by broadband dielectric spectroscopy (BDS) and electric displacement–electric field (D–E) loop measurements. Results show that 3 CN dipoles are more effective than 1 CN dipole (i.e., number density effect) in enhancing the dielectric constant and thus electrical energy storage of PIs.

EXPERIMENTAL

5.1. PI Synthesis and Film Preparation for Dielectric Characterization

The polyimide films were fabricated according to previous publications.35–37 The condensation polymerization of the diamines containing one or three nitrile dipoles with the dianhydrides being 2,2′-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA), 4,4′-oxydiphthalic dianhydride (OPDA), 4,4′-benzophenonetetracarboxylic dianhydride (BTDA), and pyromellitic dianhydride (PMDA) was conducted in N,N-dimethylacetamide (DMAc) at room temperature for 24 h to afford the corresponding poly(amic acid)s (PAA), which
were subsequently imidized by stepwise thermal treatment up to 300 °C to afford tough, creasable PI films (20–40 µm thickness).

Due to their polar nature, PIs tend to absorb a small amount of moisture, which may significantly affect their dielectric properties. Therefore, all PI films were dried in a vacuum oven at 130 °C for 24 h to remove water before any dielectric property measurements. After drying, the film samples were coated with 100 nm silver electrodes on both sides by physical vapor deposition (EvoVac Deposition System, Angstrom Engineering Inc., Kitchener, Ontario, Canada) to improve electrical contact. The electrode areas were 0.785 cm² for the BDS study and 0.0515 cm² for the $D$–$E$ loop study. The samples were then stored in a desiccator filled with Drierite until dielectric measurements were performed.

5.1. BDS Measurements

Low-voltage BDS measurements were carried out using a Novocontrol Concept 80 broadband dielectric spectrometer (Montabaur, Germany). For temperature scans, temperature was programmed to change linearly from −150 °C to 190 °C at a rate of 2 °C min⁻¹. A sine voltage of 1.0 V$_{rms}$ (root-mean square voltage) with frequency ranging from $10^7$ Hz to 1 Hz was applied across the sample film during temperature ramping, and data were recorded simultaneously. For frequency scans, samples were held at a constant temperature and the same sine voltage as above was applied with frequency ranging from $10^{-3}$ Hz to $10^7$.
Hz. High-voltage (HV) BDS experiments were carried out in the same way, except that the frequency was scanned from $10^4$ Hz to 1 Hz and the peak amplitude of the applied sinusoidal electric field was 10 and 50 MV m$^{-1}$.

5.3. $D$–$E$ Hysteresis Loop Measurements

$D$–$E$ loop measurements were performed at 23, 100, and 190 °C, using a Premier II ferroelectric tester (Radiant Technologies, Inc., Albuquerque, New Mexico, USA). The temperature was controlled by using a clean silicone oil bath equipped with an IKA RCT temperature controller (IKA Works, Inc., Wilmington, North Carolina, USA). Two consecutive sine-wave voltages with equal amplitudes were applied to the film sample and the second loop was taken as the result to eliminate the transient effect. The frequency of each wave was fixed at 10 or 1000 Hz. Stray capacitance (i.e., background capacitance from the fixture and high voltage cables) as a function of film thickness was determined by measuring the electric displacement, $D$, of biaxially oriented polypropylene (BOPP, SB Electronics, Inc., Barre, Vermont, USA) films with different thicknesses (8–55 µm) at 4000 V. The stray capacitance was subtracted from the raw data of the film sample according to its thickness.
5.4. Density Measurement

Several pieces of film samples were placed in a beaker filled with pure water and some surfactant to make sure that they sank to the bottom. After 5 min of ultrasonication to remove surface bubbles, sodium iodide was gradually added until the film samples floated (or suspended) in the solution. Then, 10 mL of the solution was sampled using a pipette and weighed to determine its density. Finally, this density was taken as the sample density.

RESULTS AND DISCUSSION

Totally, thirteen PIs were synthesized and their dielectric properties were measured. A summary of the chemical structures and the measurement results is presented in Table 5.1.
Table 5.1 Summary of measurement results of dielectric properties of the PIs.

<table>
<thead>
<tr>
<th>Group</th>
<th>Sample</th>
<th>State</th>
<th>(T_f) (°C)</th>
<th>Density (g/cm(^3))</th>
<th>RU density ((10^2\text{D}/\text{m}^3))</th>
<th>(\mu_{RU}) (D)</th>
<th>Predicted (P_{sp}) (mC/m(^2))</th>
<th>(\Delta\varepsilon_r) (BDS)</th>
<th>Exp. (P_{sp}) (mC/m(^2))</th>
<th>(P_{sp}) ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6FDA-mmDAm (CP2)</td>
<td>Am</td>
<td>199</td>
<td>1.433</td>
<td>1.23</td>
<td>0.28</td>
<td>0.0056</td>
<td>0.054</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>a. OPDA-mmDAmCN</td>
<td>Am</td>
<td>255</td>
<td>1.367</td>
<td>1.30</td>
<td>5.32</td>
<td>2.27</td>
<td>0.635</td>
<td>0.36</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>b. OPDA-mmDAmCN</td>
<td>Am</td>
<td>240</td>
<td>1.367</td>
<td>1.39</td>
<td>5.32</td>
<td>2.27</td>
<td>0.413</td>
<td>0.32</td>
<td>0.14</td>
</tr>
<tr>
<td>3</td>
<td>a. PMDA-ppDAmCN</td>
<td>Cryst (high)</td>
<td>341</td>
<td>1.357</td>
<td>1.11</td>
<td>17.1</td>
<td>17.9</td>
<td>1.372</td>
<td>0.87</td>
<td>0.048</td>
</tr>
<tr>
<td></td>
<td>b. PMDA-mmDAmCN</td>
<td>Cryst (high)</td>
<td>305</td>
<td>1.367</td>
<td>1.12</td>
<td>17.1</td>
<td>18.0</td>
<td>0.644</td>
<td>0.85</td>
<td>0.047</td>
</tr>
<tr>
<td>4</td>
<td>a. OPDA-ppDAmCN</td>
<td>Cryst (low)</td>
<td>235</td>
<td>1.342</td>
<td>0.98</td>
<td>16.0</td>
<td>13.9</td>
<td>1.139</td>
<td>0.83</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td>b. OPDA-mmDAmCN</td>
<td>Cryst (low)</td>
<td>229</td>
<td>1.342</td>
<td>0.98</td>
<td>16.0</td>
<td>13.9</td>
<td>0.850</td>
<td>0.46</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>c. OPDA-mmDAmCN</td>
<td>Am</td>
<td>216</td>
<td>1.342</td>
<td>0.98</td>
<td>16.0</td>
<td>13.2</td>
<td>0.761</td>
<td>0.12</td>
<td>0.008</td>
</tr>
<tr>
<td>5</td>
<td>a. 6FDA-ppDAmCN</td>
<td>Am</td>
<td>244</td>
<td>1.388</td>
<td>0.87</td>
<td>15.1</td>
<td>11.1</td>
<td>0.850</td>
<td>0.60</td>
<td>0.054</td>
</tr>
<tr>
<td></td>
<td>b. 6FDA-mmDAmCN</td>
<td>Am</td>
<td>232</td>
<td>1.400</td>
<td>0.88</td>
<td>15.1</td>
<td>11.2</td>
<td>0.921</td>
<td>0.64</td>
<td>0.058</td>
</tr>
<tr>
<td></td>
<td>c. 6FDA-mmDAmCN</td>
<td>Am</td>
<td>226</td>
<td>1.400</td>
<td>0.88</td>
<td>15.1</td>
<td>11.2</td>
<td>0.486</td>
<td>0.49</td>
<td>0.044</td>
</tr>
<tr>
<td>6</td>
<td>a. BTDA-mmDAmCN</td>
<td>Am</td>
<td>238</td>
<td>1.357</td>
<td>0.98</td>
<td>14.1</td>
<td>10.9</td>
<td>0.583</td>
<td>0.49</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>b. BTDA-mmDAmCN</td>
<td>Am</td>
<td>218</td>
<td>1.344</td>
<td>0.97</td>
<td>14.1</td>
<td>10.8</td>
<td>0.427</td>
<td>0.25</td>
<td>0.023</td>
</tr>
</tbody>
</table>

\(^a\) The state of PI films was determined by X-ray diffraction (XRD) and comparing the transmission- and reflection-mode XRD spectra, which are shown in Section I of Appendix 1. \(^b\) The dipole moment of the repeat unit \((\mu_{RU})\) is calculated by the absolute value of diamine dipole moment minus dianhydride dipole moment. The dipole moments of diphenyl ether, 1,1,1,3,3,3 hexafluoropropane, benzophenone, and benzonitrile are 1.14, 2.0, 2.96, and 4.18 D, respectively. \(^c\) \(\Delta\varepsilon_r\) is the difference between the real part of relative permittivity at 190 °C and 1 kHz and that at −150 °C and 1 kHz. Since at −150 °C only electronic and atomic polarizations contribute to permittivity while at 190 °C dipole vibration also contributes, the difference of relative permittivity between the two temperatures can be attributed solely to the dipolar polarization. \(^d\) Experimental polarization only due to dipole orientation. This is calculated as: \(D–E\) loop polarization at 190 °C and 1 kHz minus polarization from BDS at −150 °C and 100 kHz, extrapolated to a field of 100 MV m\(^{-1}\).
5.5. Effect of the Number of –CN Groups in the Diamine Part of PI

To investigate the effect of the number of nitrile groups in the diamine part of the PIs on dielectric properties, we selected three PIs from the list in Table 5.1. They are 1, 2b, and 4c, which contain 0, 1, and 3 nitrile groups, respectively. Due to limitation of available PIs, the dianhydride part in sample 1 is different from those in samples 2b and 4c. Fig. 5.1 shows the real ($\varepsilon'_r$) and imaginary ($\varepsilon''_r$) parts of relative permittivity and the dissipation factor (tan $\delta$) as a function of temperature for samples 1, 2b, and 4c. At $-150$ °C (see Fig. 5.1A, D, and G), $\varepsilon'_r$ increased as the number of nitrile groups increased, from 2.93 for 1 to 3.30 for 2b, and to 3.60 for 4c. We shall now try to determine the origins of this increase in $\varepsilon'_r$. Even though it might seem as if the increase in $\varepsilon'_r$ arises exclusively from the added nitrile groups, this has to be verified because 1, 2b and 4c all have slightly different structures. At such a low temperature ($-150$ °C), the contribution from impurity ion migration to the relative permittivity could be ignored. Therefore, $\varepsilon'_r$ itself should only originate from electronic, atomic (or vibrational), and dipolar polarizations. It is possible to accurately (usually within 1% error) predict the electronic component of the permittivity, $\varepsilon_{r,e}$, using the Lorentz–Lorenz relationship that relates molar refraction $R_M$ to permittivity:

$$R_M = \frac{\varepsilon_{r,e} - 1}{\varepsilon_{r,e} + 2} \frac{M_{RU}}{\rho} = \frac{N_A}{3\varepsilon_0} \alpha_e$$

(5.1)

where $M_{RU}$ is the molar mass of the repeat unit, $\rho$ is the bulk density of the PI, $N_A$ is the Avogadro constant, $\varepsilon_0$ is the vacuum permittivity, and $\alpha_e$ is the electronic polarizability. In this case, the molar refraction is that of the repeat unit of the PI.
Molar refraction is obtained by adding up molar refractions of individual bonds (i.e., bond refractions\(^{39,40}\)) in the repeat unit. The molar refraction for sample 1 is calculated to be 158.5 cm\(^3\) mol\(^{-1}\) and the permittivity obtained for sample 1 from electronic polarization is 2.44 (see Section II of Appendix 1 for calculations). This calculated value, however, is somewhat lower than the experimental value of 2.93, because it does not include vibrational and dipolar polarizations. From Fig. 5.1A, we can see that the contribution from dipolar polarization is insignificant, because the permittivity changes little (only 0.05 at 1 kHz) from \(-150^\circ\)C to 190 °C, compared to samples 2b and 4c which contain added nitrile groups. If we assume zero dipolar contribution to permittivity, the difference between the measured and calculated permittivity, namely 0.49, should arise from vibrational polarization for sample 1, according to the Clausius–Mossotti relations:\(^{39}\)

\[
\frac{\varepsilon_r^{-1} M_{RU}}{\varepsilon_r+2} \rho = \frac{N_A}{3\varepsilon_0} (\alpha_e + \alpha_v) \tag{5.2}
\]

where \(\varepsilon_r\) has contributions from both \(\alpha_e\) and vibrational polarizability \(\alpha_v\). In other words, the magnitude of vibrational polarization is about 20% of that of the electronic polarization for sample 1. This percentage is similar to what has been reported for polymers in general.\(^{39,41}\) Since the structures of samples 2b and 4c are similar to sample 1 except the nitrile groups, we assume that the percentage of vibrational polarization relative to electronic polarization is also 20% for them. Based on bond refractions,\(^{39,40}\) the molar refraction for sample 2b is calculated to be 152.2 cm\(^3\) mol\(^{-1}\). Taking into account the 20% vibrational polarization, the permittivity \(\varepsilon_r\) from electronic and vibrational polarizations can be calculated to be 3.15. Compared with the experimental \(\varepsilon'_r\) of 3.30, the contribution from dipolar
polarization must be 0.15 for sample 2b at −150 °C. Following the same calculation method, sample 4c has a molar refraction of 212.9 cm³ mol⁻¹ and a contribution to permittivity of 0.50 from dipolar polarization. This makes sense because 4c has 3 CN dipoles per repeat unit as opposed to 1 CN dipole for sample 2b, and a contribution of 0.50 from dipole motions for 4c is approximately 3 times higher than that of 0.15 for sample 2b. We can therefore conclude that the permittivity increase at −150 °C from sample 1 to 2b, and finally to 4c originates from dipolar polarization.

![Fig. 5.1.](image-url)  

ε′, ε″, and tanδ as a function of temperature for samples 1, 2b, and 4c, which contain 0, 1, and 3-CN groups, respectively.
Upon increasing temperature from $-150 \degree C$ to $190 \degree C$, both $\varepsilon'$ and $\varepsilon''$ increased for all three samples. These increases could be attributed to the enhanced dipole motion as temperature increased. Because the glass transition temperatures ($T_g$s) for these samples are above 200 $\degree C$ (see Table 5.1), contribution from impurity ion migration to this increase in permittivity might be ignored for frequencies above 10 Hz. From the $\varepsilon''$ plots for CN-containing samples (Fig. 5.1E and H), weak $\gamma$ transition peaks were noticed at around $-85 \degree C$ at 1 Hz. Similar relaxation peaks were also seen for other CN-containing samples (see Fig. 5.4, 5.6, and 5.8 later). These peaks could arise from absorbed water in the samples; although our samples had been dried in a vacuum oven at 130 $\degree C$ for at least 24 h before testing, it was fairly difficult to completely eliminate trace amounts of absorbed moisture because all samples contained polar $–CN$ groups. A similar phenomenon was also reported for Kapton, namely, a trace amount of absorbed moisture produced a relaxation peak around $-100 \degree C$.$^{38}$ For low frequency $\varepsilon''$ and tan $\delta$ plots (Fig. 5.1E/F and H/I), another relatively broad relaxation peak was observed around 150–180 $\degree C$ for samples 2b and 4c (and all other CN-containing samples; see Fig. 5.4, 5.6, and 5.8 later). This peak could be assigned to the $\beta$ relaxation, which is often due to the onset of dipole motions that are precursors to the long-range segmental motions in the $\alpha$ relaxation (or glass transition). To avoid significant deformation of samples, the upper temperature limit was chosen as 190 $\degree C$.

Fig. 5.2A compares the increase of $\varepsilon'$ from $-150 \degree C$ to $190 \degree C$ for samples 1, 2b, and 4c at different frequencies, i.e., $\Delta \varepsilon' = \varepsilon' (190 \degree C) - \varepsilon' (-150 \degree C)$. Since
electronic and vibrational polarizations did not change much with temperature,\textsuperscript{39,42} \( \Delta \varepsilon'_r \) could be attributed to the change in dipolar polarization only. Clearly, adding more CN dipoles into the PI structure increased \( \Delta \varepsilon'_r \). For example, sample 1 did not contain any CN dipoles and its \( \Delta \varepsilon'_r \) was only about 0.05 at 1 kHz. Sample 2b contained 1 CN dipole and its \( \Delta \varepsilon'_r \) increased to 0.41 at 1 kHz. Sample 4c contained 3 CN dipoles and its \( \Delta \varepsilon'_r \) increased to 0.76 at 1 kHz.

**Fig. 5.2.** (A) Increase of the real part of permittivity, \( \Delta \varepsilon'_r \), and (B) tan\( \delta \) at 190 °C at 10\(^3\), 10\(^4\), and 10\(^5\) Hz for samples 1, 2b, and 4c.

The effect of added CN dipoles could be better understood by predicting the polarization from permanent dipoles in the sample. Assuming each repeat unit adopts an anti-parallel configuration, \textit{i.e.}, dianhydride and diamine dipoles orient in the opposite directions (see the chemical structures in Table 5.1; the dianhydride dipole moment is pointing down and the diamine dipole moment is pointing up), without external electric field, the net dipole moment of each repeat unit (\( \mu_{RU} \)) can be calculated by subtracting the dianhydride dipole moment from the diamine dipole moment. According to the literature, dipole moments of
diphenyl ether,\textsuperscript{43} 1,1,1,3,3,3-hexafluoropropane,\textsuperscript{44} benzophenone,\textsuperscript{45} and benzonitrile\textsuperscript{46} are 1.14, 2.0, 2.96, and 4.18 Debye (D), respectively. The dianhydride dipole moments increase in the order PMDA (0 D) \textless BTDA (14.14 D) \textless 6FDA (15.10 D) \textless OPDA (15.96 D). Samples \textbf{3a, 4a, 5a,} and \textbf{6a} contain these dianhydrides in this exact order (see results later), and they all have identical diamine parts, meaning that their total dipole moments would decrease from \textbf{3a–6a} as the dianhydride dipole moment increases. From the permittivity increase \(\Delta\varepsilon_r\) from dipolar polarization (Table 5.1), \(\Delta\varepsilon_r\) indeed decreases in the order of \textbf{3a} > \textbf{4a} > \textbf{5a} > \textbf{6a}. Therefore, it is reasonable to assume that the diamine and dianhydride parts are antiparallel in the samples.

Presently, there is no explicit theoretical prediction of dipolar polarization for main-chain polymers containing permanent dipoles, and here we resort to a freely rotating dipole model. Assuming the net dipole moment of each repeat unit, \(\mu_{RU}\), can freely rotate as a single dipole, the predicted polarization from dipole orientation \((P_{dip})\) is:\textsuperscript{39}

\[
P_{dip} = N\mu_{RU} \left( \coth u - \frac{1}{u} \right), \text{ here } u = \frac{\mu_{RU}E}{k_BT}
\]

(5.3)

where \(N\) is the repeat unit density, \(\mu_{RU}\) the dipole moment of a repeat unit, \(E\) the applied electric field, \(k_B\) the Boltzmann constant, and \(T\) the absolute temperature. Supposedly, \(E\) should be the local electric field for the freely rotating dipole. However, there have been debates on the prediction of local field for polar materials with freely rotating permanent dipoles.\textsuperscript{47} It is considered that the local field should be inappreciably different from the external electric field. Therefore, we use the applied electric field here. On the basis of these assumptions, the
predicted polarizations from freely rotational permanent dipoles were calculated to be 0.0056, 2.27, and 13.9 mC m$^{-2}$ for samples 1, 2b, and 4c, respectively (see Table 5.1). Obviously, adding more CN dipoles into PI samples increased the dipolar polarization, and thus $\Delta \varepsilon'$, followed exactly the trend of dipolar polarization for samples 1, 2b, and 4c. Nonetheless, as the permittivity increased, the dielectric loss ($\tan \delta$) at 10$^3$ to 10$^5$ Hz also increased proportionally (Fig. 5.2B). For polar polymers, loss mechanisms include dipole relaxation loss, impurity-ion migration loss, and electronic (or DC) conduction loss. Below, we will discuss the loss mechanisms in these PI samples.

Fig. 5.3 shows frequency-scan plots of $\varepsilon'$ and $\varepsilon''$ for samples 1, 2b, and 4c at $-150$ °C, 25 °C, and 190 °C. At $-150$ °C (Fig. 5.3A and D), $\varepsilon'$ increased with added –CN groups and remained nearly independent of frequency for all samples. Meanwhile, $\varepsilon''$, stayed relatively low, between 10$^{-3}$ and 10$^{-2}$ (i.e., $\tan \delta$ between 3 x 10$^{-4}$ and 3 x 10$^{-3}$). However, these $\tan \delta$ values were still higher than the dissipation factor for BOPP, which is around 1 x 10$^{-5}$ at $-150$ °C.$^{48}$ At such low temperatures, both impurity-ion migration loss and electronic conduction loss could be negligible. Generally speaking, no dipole flipping should occur below the lowest sub-$T_g$ transition temperature. However in this case, molecular motion could not be completely frozen at $-150$ °C and it was still possible for dipoles to wiggle even at such a low temperature, causing higher loss than in nonpolar, linear dielectric polymers such as BOPP.
Fig. 5.3. Frequency-scan $\varepsilon'$ and $\varepsilon''$ plots for samples 1, 2b, and 4c at -150 °C (A and D), 25 °C (B and E), and 190 °C (C and F), respectively.

Regarding sample 1 which contained no –CN dipoles, when the temperature increased from -150 °C to 25 °C and to 190 °C, there was no obvious increase in $\varepsilon'$ at low frequencies (<1 Hz; see Fig. 5.3A–C). This differed from samples 2b and 4c that contained CN dipoles. At 25 °C, $\varepsilon'$ for samples 2b and 4c showed a slight increase in the low frequency region (<1 Hz), while for all samples, $\varepsilon''$ continuously increased with decreasing frequency, going from 0.002 to 0.03 and the loss mechanism was again primarily attributed to dipole motion. As the temperature increased to 190 °C, $\varepsilon'$ for samples 2b and 4c had a stepwise decrease and $\varepsilon''$ showed a weak and broad dipole relaxation peak around $10^3$ Hz with an upturn at frequencies below 1 Hz. Since the low frequency upturn has a slope close to -1, we attribute it to the impurity-ion migration loss.49,50
From the above results, we conclude that adding CN dipoles to the PI main chain primarily gives rise to two effects. First, it introduces dipolar motion (e.g. wiggling) into the PI sample. Because the –CN groups are directly attached to the main chain in a 90° configuration, this motion seems to be hindered and will cause significant friction with randomly packed neighboring chains. As a result, together with an increase in $\varepsilon'$, there is also an increase in $\varepsilon''$, due to the dipoles trying to rotate the main chain. This explains the trend in Fig. 5.2 that both $\varepsilon'$ and $\varepsilon''$ increase with adding –CN groups into the PI structure. Second, by adding –CN groups, the PI samples become more polar and are easily contaminated with impurity ions with enhanced ion mobility. At high enough temperature and low enough frequency, impurity-ion migration loss becomes significant (see Fig. 5.3F). For the low-field BDS spectra in Fig. 5.1 and 5.3, the applied voltage is so low ($1 V_{rms}$) that electronic conduction may be ignored.$^{51}$

5.6. PI Samples with a para–para Linkage in the Diamine

From the above dielectric property measurements, we learned that PI samples with 3 nitrile groups showed high permittivity due to dipolar polarization. Below, we will focus on the PI samples containing 3 nitrile groups (see Table 5.1). These samples are divided into four groups based on the dianhydride part of the PI repeat unit, so each group only contains PIs with the same dianhydride part. The dianhydride parts for groups 3–6 are PMDA, OPDA, 6FDA, and BTDA, respectively. The diamine (DAm) part contains a para–para (pp), meta–para
(mp), or a \textit{meta–meta} (mm) linkage to the dianhydride part. Below, we will compare the dielectric properties of PI samples having the \textit{para–para} linkage in the diamine part.

Fig. 5.4 shows temperature-scan BDS spectra for samples 3a, 4a, 5a, and 6a. For these samples, the $\epsilon'$ slightly fluctuated around 3.5 at $-150$ °C, likely due to different responses from different dianhydride parts in the samples. Upon raising the temperature from $-150$ °C to 190 °C, $\epsilon'$ showed a significant increase above ca. 50 °C. However, the amounts of increase, $\Delta \epsilon'$, at $10^3$, $10^4$, and $10^5$ Hz are different for these samples (see Fig. 5.5A). Basically, $\Delta \epsilon'$ decreased consistently from 3a to 6a, which again could be attributed to the decrease of the predicted $P_{\text{dip}}$ (see Table 5.1), which in turn could be associated with the rigidity of the polymer chain. For example, $P_{\text{dip}}$ decreased from 17.9 mC m$^{-2}$ for 3a to 13.9 mC m$^{-2}$ for 4a, to 11.1 mC m$^{-2}$ for 5a, and finally to 10.9 mC m$^{-2}$ for 6a.
Fig. 5.4. Temperature-scan plots of $\varepsilon_r'$, $\varepsilon_r''$, and tan$\delta$ for samples 3a, 4a, 5a, and 6a with a para-para linkage in the diamine part.
For samples 3a through 6a, γ transitions were observed around −100 °C in $\varepsilon''$ and tan δ plots in Fig. 5.4. This could again be attributed to either dipolar group relaxation in the polymer or to the absorbed moisture. Meanwhile, a broad β relaxation shoulder peak was observed in $\varepsilon''$, at 1 Hz around 100–150 °C, and with increasing the frequency it moved to higher temperatures.

A comparison of tan δ values at $10^3$ to $10^5$ Hz for samples 3a–6a is shown in Fig. 5.5B. As we can see, a higher tan δ value in Fig. 5.5B also coincided with a higher $\Delta\varepsilon'_r$ value in Fig. 5.5A. From the above discussion, we understood that larger dipole motions resulted in a higher $\Delta\varepsilon'_r$, which in turn also resulted in a higher tan δ, because the CN dipoles were directly attached to the PI main chain.

### 5.7. PI Samples with a meta–para Linkage in the Diamine

Fig. 5.6 shows the temperature-scan dielectric spectra of $\varepsilon'_r$, $\varepsilon''$, and tan δ for samples 4b and 5b with a meta–para linkage in the diamine. Similar results
were obtained compared with the above PI samples with a para–para linkage in the diamine. At −150 °C, $\varepsilon'$ was about 3.63 and 3.25 for samples 4b and 5b, respectively. With increasing the temperature up to 190 °C, $\varepsilon'$ increased continuously. In the $\varepsilon''$ and tan $\delta$ plots, the $\gamma$ relaxation peak was seen at −100 °C and the $\beta$ shoulder was seen at 100–150 °C at a frequency of 1 Hz. With increasing the frequency, both relaxation peaks shifted to higher temperatures. Both $\Delta\varepsilon'$ and tan $\delta$ were similar for 4b and 5b, as shown in Fig. 5.7.

**Fig. 5.6.** Temperature-scan plots of $\varepsilon'_r$, $\varepsilon''_r$, and tan$\delta$ for samples 4b and 5b with a meta-para linkage in the diamine.
Fig. 5.7. (A) Increase of the real part of permittivity, $\Delta \epsilon'$, and (B) $\tan \delta$ at 190 °C at $10^3$, $10^4$, and $10^5$ Hz for samples 4b and 5b with a meta-para linkage in the diamine.

5.8. PI Samples with a meta–meta Linkage in the Diamine

Fig. 5.8 shows the temperature-scan dielectric spectra of $\epsilon'$, $\epsilon''$, and $\tan \delta$ for samples 3b, 4c, 5c, and 6b with a meta–meta linkage in the diamine. Again, similar results were obtained compared with PI samples with para–para and meta–para linkages in the diamine. The $\epsilon'$ values at −150 °C were around 3.5 for these samples, except for sample 5c, whose $\epsilon'$ was ca. 3.15. With increasing temperature from −150 °C to 190 °C, $\epsilon'$ increased continuously. From the $\epsilon''$ and $\tan \delta$ plots, the γ relaxation peak was seen at ca. −80 °C and the β shoulder was seen around 100–150 °C for the 1 Hz curve. With increasing the frequency, both relaxation peaks shifted to higher temperatures.
Fig. 5.8. Temperature-scan plots of $\varepsilon_r'$, $\varepsilon_r''$, and tan$\delta$ for samples 3b, 4c, 5c, and 6b with a meta-meta linkage in the diamine.

Fig. 5.9 shows a comparison of $\Delta\varepsilon_r'$ and tan $\delta$ for samples 3b, 4c, 5c, and 6b. The $\Delta\varepsilon_r'$ decreased from sample 3b to 6b. This was understandable because the predicted $P_{\text{dip}}$ decreased from 18.0 mC m$^{-2}$ for 3b to 13.2 mC m$^{-2}$ for 4c, to 11.2 for 5c and finally to 10.8 for 6b. Meanwhile, tan $\delta$ also decreased from 3b to
6b, because the higher predicted $P_{dip}$ from CN dipoles directly attached to the main chain would result in a higher loss.

![Graph showing the real part of permittivity and tanδ](image)

**Fig. 5.9.** (A) Increase of the real part of permittivity, $\Delta \varepsilon'_r$, and (B) tanδ at 190 °C at $10^3$, $10^4$, and $10^5$ Hz for samples 3b, 4c, 5c, and 6b with a meta-meta linkage in the diamine.

### 5.9. Effect of Diamine Linkage Type on $\Delta \varepsilon'_r$

From the above results, we learned that the dipole moment of a repeat unit played an important role in enhancing the $\Delta \varepsilon'_r$. Meanwhile, we noticed that the type of linkage in the diamine also affects the $\Delta \varepsilon'_r$. From Fig. 5.10, the general trend for groups 3–6 was that the $\Delta \varepsilon'_r$ decreased from para–para to meta–para, and to meta–meta regarding the type of linkage in the diamine, regardless of whether the frequency was 1 kHz or 100 kHz. This indicates that the para–para linkage in the diamine containing 3 CN dipoles could rotate more easily than the meta–para and meta–meta linkages.
Fig. 5.10. Increase of the real part of permittivity, $\Delta \varepsilon_r'$, at (A) 1 kHz and (B) 100 kHz for groups 3-6 with different types of linkage in diamines: para-para (ppDAm), meta-para (mpDAm), and meta-meta (mmDAm). Connecting lines are shown to guide the eye.

5.10. Electrical Energy Storage Studied by $D-E$ Loops

In the above studies, we have focused on linear dielectric properties at low electric fields. In practice, polymer dielectrics are often used at high electric fields. For example, BOPP film DC-link capacitors in electric vehicles often operate at 200 MV m$^{-1}$ and at a frequency of 10–20 kHz.$^8$ Therefore, it is highly desired to investigate high-field dielectric properties of the PI samples in Table 5.1. Here, we employ both $D-E$ hysteresis loop and high-field BDS studies. Fig. 5.11 shows typical $D-E$ loops under a poling field of 100 MV m$^{-1}$ for various PI samples in Table 5.1, together with Kapton and Ultem for comparison. In general, one could obtain useful information on high-field dielectric properties from $D-E$ loops. In this study, for example, the slope of the loop (i.e., $D_{\text{max}}/E_{\text{max}}$) gave the apparent dielectric constant; the charged and discharged energy densities ($U_e$) were obtained from $U_e = \int E dD$ of the respective charging and discharging
The loss mechanisms again include electronic conduction, impurity ion migration, and dipole motion. From a recent report, we understand that electronic conduction shifts up the upper half of the $D-E$ loop, and impurity ionic migration and dipole switching broaden the loop symmetrically and increase the slope as well. Therefore, the loss from electronic conduction can be deconvoluted. However, it is fairly difficult to deconvolute contributions from impurity ions and dipoles in one $D-E$ loop. One way to circumvent this difficulty is to run $D-E$ loops at a high enough frequency ($e.g.$, 1 kHz or above) so that the contribution from impurity ion migration could be minimized, because relaxation for amorphous dipoles usually occurs above 1 kHz whereas impurity ions in polymers are often slow, $e.g.$, below 1 kHz. Examples of dipolar and impurity ion losses have been discussed in Fig. 5.3C and 5.3F.
Fig. 5.11. Bipolar $D$-$E$ hysteresis loops for various polyimides in Table 5.1, together with Kapton and Ultem, measured at $10$ Hz and $1$ kHz (where noted).
From Fig. 5.11, PI samples without any CN dipoles, such as 1, Kapton, and Ultem, exhibited narrow loops, no matter what the frequencies and temperatures. This is the advantage of linear dielectric polymers. On the other hand, PI samples with CN dipoles exhibited broader loops. Below, we will discuss the different loss mechanisms for CN-containing PI samples. Careful inspection of $D$–$E$ loops for CN-containing PI samples indicated that electronic conduction loss was not a significant loss mechanism for the PI samples because most loops (except that of 2b, which may result from defects such as pin-holes in the sample) were symmetrical about the electric field axis. We consider that electron traps in these PI samples were effective in preventing the hopping mechanism of electron conduction when the temperature was below the $T_g$. At 100 °C, all $D$–$E$ loops at the poling frequency of 10 Hz appeared relatively narrow, indicating that electron traps were effective at a temperature of at least 100 °C below the $T_g$. At 190 °C and 1 kHz, the $D$–$E$ loops appeared slightly broader than those at 100 °C and 10 Hz. Considering the dipole relaxation peak at 190 °C around 1 kHz (Fig. 5.3F), the loss mechanism at 190 °C and 1 kHz should be attributed to dipole wiggling in the CN-containing PI samples. However, the loops measured at 190 °C and 10 Hz (shown in red) had a steeper slope than those measured at 190 °C and 1 kHz. This could be attributed to additional impurity ion migration in the samples because migration of impurity ions increases the loss (i.e., broader loops) and the accumulation of these ions at both electrodes increases the capacitance and thus the slope of the $D$–$E$ loops. On the basis of our previous reports, less than ppm level of impurity
ions could cause significant impurity-ion migration loss.\textsuperscript{51}

To understand the effect of dipolar polarization, we had to exclude the loss mechanism due to impurity ions. As we mentioned above, running $D$–$E$ loops at 1 kHz could possibly eliminate the influence from impurity ions because their motion is slower than that of dipoles. From the $D$–$E$ loops at 190 °C and 1 kHz, an apparent dielectric constant could be obtained. If we assume that the permittivity at −150 °C and 100 kHz in the BDS study originated solely from deformational (\textit{i.e.}, electronic and vibrational) polarization, the polarization from dipoles could be obtained from the difference between the $D$–$E$ loop apparent dielectric constant at 190 °C and 1 kHz and the BDS permittivity at −150 °C and 100 kHz. Table 5.1 lists the experimental $P_{dip}$ values for different PI samples. The ratio between experimental $P_{dip}$ and predicted $P_{dip}$ could be an indicator of dipole wiggling in the PI samples at 190 °C. For samples containing 1 nitrile group, the ratio was about 0.15, whereas for samples containing 3 nitrile groups, the ratio was only around 0.05. This suggested that fixing CN dipoles onto rigid PI main chains significantly decreased their mobility, compared with the freely rotating model (see eqn (5.3)). In addition, introducing more CN dipoles onto the PI main chain further increased the polymer rigidity.

The discharged energy densities and loss\% at an applied field of 100 MV m\textsuperscript{−1} were obtained from $D$–$E$ loops for all samples, and results are summarized in Fig. 5.12 and 5.13. Samples 3a and 3b exhibited the highest discharged energy density with reasonably low loss\%.
Fig. 5.12. Discharged energy density of different samples from DE-loop measurements at 100 MV/m at different temperatures and frequencies.

Fig. 5.13. Hysteresis loop loss% from D-E loop measurements at 100 MV/m at different temperatures and frequencies for different samples.
PI samples without any nitrile groups had the lowest loss%; however, their discharged energy densities were also the lowest. For example, the discharged energy density for 3a at 190 °C and 10 Hz was about 1.9 times those of samples 1, Kapton, and Ultem (see Fig. 5.12). From Fig. 5.13, the closer the heights of the red (190 °C and 10 Hz) and blue (190 °C and 1 kHz) bars, the less ionic and electronic conduction loss because the loss% at 190 °C and 10 Hz included losses from impurity ion migration and dipole motion, whereas the loss% at 190 °C and 1 kHz should be exclusively due to dipole motion.

5.11. High Voltage BDS Study

In addition to $D-E$ loops, high-field dielectric properties were also studied using HV BDS, and the results for samples 3b and 5a are shown in Fig. 5.14. These results look similar to the low-field BDS spectra; however, there are differences. First, the $\epsilon'_r$ values at −150 °C for both samples were around 3.5 and increased with increasing temperature. The difference was that the $\Delta\epsilon'_r$ at 1 kHz was higher for HV BDS than for normal BDS. For example, $\Delta\epsilon'_r$ was 1.25 and 1.06 in HV BDS, whereas it was 0.62 and 0.87 in low-field BDS for samples 3b and 5a, respectively. Second, $\gamma$ and $\beta$ relaxation peaks were also observed in HV BDS $\epsilon''_r$ plots for samples 3b and 5a. However, the $\epsilon''_r$ values were much higher in HV BDS than those in low-field BDS. This could be attributed to enhanced electronic conduction, impurity ion migration, and dipole motion under high electric fields.
As we can see from Table 5.1, the fraction of dipole flipping for most of the samples is only about 0.05. This can be explained by the rigid structure of the PIs, which does not allow dipoles to turn. This rigid structure of course is what imparts great thermal stability to PIs. Also, from Fig. 5.2B, dielectric losses increase with the addition of CN dipoles. Since the CN dipoles are attached to the main chain of the PIs in all samples studied, the chain needs to turn with the CN dipoles when an electric field is applied. The result is obvious: the dipoles are difficult to turn because they need to turn part of the rigid main chain. However, small amplitude turning may still occur, but is hampered by strong frictional
forces giving rise to relatively high losses. To solve this problem of low dipole turning and high loss, the dipoles should not be attached directly to the PI main chain. Bendler et al.\textsuperscript{28} reported a study attaching cyanomethylene groups to bisphenol A polycarbonate (PC), having a CH\textsubscript{2} group between the main chain and the nitrile group so that the dipole could rotate more freely in the side group. The CN-modified PC achieved a polarization fraction of 0.10 of the theoretical prediction and a dielectric constant of 4.0. In future, we plan to attach –CH\textsubscript{2}CN groups to PIs in order to enhance the dipole mobility but keep the dipolar loss low.

**CONCLUSIONS**

In this work, we systematically investigated a series of PI samples containing highly polar nitrile groups. BDS and $D$–$E$ loop results indicated that adding CN dipoles into PI structures increased the permittivity. Especially on the diamine unit basis, 3 nitrile groups were more effective than 1 nitrile group in increasing the permittivity. Among polar PI samples having 3 nitrile groups, the dipole moment of the dianhydride also played an important role. With increasing the dipole moment of the dianhydride part in the order of PMDA, OPDA, 6FDA, and BTDA, the enhancement of permittivity gradually decreased. This suggested that the dianhydride and diamine should arrange in an opposite direction with dipole moments cancelling each other on the molecular scale. In addition, \textit{para–para} linkage in the diamine yielded a higher permittivity than \textit{meta–para} and
meta-meta linkages between dianhydride and diamine parts due to easier rotation around the para–para bonds. From the high-field D–E loop study, discharged energy density and loss% were obtained. Sample 3a exhibited the highest discharged energy density due to its high dipolar polarization. From the HV BDS study, even higher permittivities were observed.

Although enhanced permittivity was achieved for these CN-containing PI samples, dielectric losses, i.e., tan δ and loss%, were also increased. This could be attributed to the fact that CN dipoles were directly attached to the PI main chain. In a recent study, the nitrile group was attached to the bisphenol-A unit of PC via a methylene group. The rotation of the acetonitrile side group became easier than the nitrilephenyl main chain in our PI samples. In future, we will synthesize PI samples with a polarizable side group such as –CH₂CN in order to achieve higher permittivity and electrical energy storage while maintaining a low dielectric loss.

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PART II

CHAPTER 1


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ABSTRACT

A porous Teflon ring/solid disk electrode is herein described specifically designed for acquiring online mass spectrometric measurements under well-defined forced convection created by liquid emerging from a circular nozzle impinging on the disk under wall-jet conditions. Measurements were performed for the oxidation of hydrazine, N$_2$H$_4$, in a deaerated phosphate buffer electrolyte (pH 7) on Au, a process known to yield dinitrogen as the product. The N$_2^+$ ion currents, measured by the mass spectrometer, $i(N_2^+)$, as well as the corresponding polarization curves recorded simultaneously displayed very similar
s-like shapes when plotted as a function of the potential applied to the Au disk. In fact, the limiting currents observed both electrochemically and spectrometrically were found to be proportional to \([N_2H_4]\). However, the limiting values of \(i(N_2^+)\) did not increase monotonically with the flow rate, \(\nu_f\), reaching instead a maximum and then decreasing to values independent of \(\nu_f\). This behavior has been attributed in part to hindrances in the mass transport of gases through the porous materials.

**INTRODUCTION**

Since its inception about 4 decades ago,(1) the coupling of electrochemical systems with online mass spectrometry has provided valuable information regarding the mechanism of a growing number of reactions of fundamental and applied interest.(2, 3) A variety of cell configurations have been devised allowing in most cases gases generated either directly or indirectly by electrochemical reactions to permeate through a porous membrane or plug, mostly made of Teflon, into an evacuated chamber that houses the mass spectrometer.(1, 3-15) Of particular relevance to this work are strategies that combine the virtues of mass spectrometry with those of mass transport of the liquid electrolyte under forced convection.(5, 7, 9, 11, 12) Efforts in this direction have been reported by Tegtmeyer et al.,(9) who described a rotating porous metal disk electrode and established correlations between the Faradaic current and the ion current measured by the mass spectrometer, which were then used
to calculate collection efficiencies. More recently, Heinen et al.(6) coupled online
differential electrochemical mass spectrometry (DEMS) with in situ attenuated
total reflection infrared spectroscopy in a channel-type dual thin-layer
electrochemical flow-cell allowing simultaneous detection of gas phase products
as well as stable solution phase and reactive adsorbed species. Directly relevant
to our work is the report of Wang et al.,(11) who developed a double-band
electrode channel cell, separated by a coplanar porous Teflon membrane. This
arrangement made it possible to monitor not only gases but also
electrochemically generated electroactive species.

The present contribution describes a novel assembly that enables gaseous
species produced at a solid Au disk electrode under well-defined jet impinging
conditions to permeate through a concentric porous Teflon ring membrane
supported on a porous Teflon annulus, into the mass spectrometer chamber. The
virtues of this device have been illustrated using the oxidation of hydrazine, \( \text{N}_2\text{H}_4 \),
in an aqueous electrolyte, a process known to yield dinitrogen as the product.(15, 16)

**EXPERIMENTAL**

The ring-disk probe specifically designed for online mass spectrometric
measurements under well-defined forced convection generated by a jet
impinging electrolyte consists of four main components (see panel A, Figure II.1):
a solid Au cylinder 0.5 cm in diameter (area, 0.196 cm\(^2\)) and 0.75 cm in height, a
Teflon membrane (80 µm thick, thread seal tape from Fel-Pro Inc.), which was stretched to form a disk about 2 cm in diameter, a porous PTFE annulus (1–2 µm pore size, Porex) of outer diameter, 0.73 cm, inner diameter, 0.45 cm, and a solid PTFE holder in the form of a hollow cylinder (1.75 cm outer diameter, 4.6 cm long). The porous annulus was cut out from a 0.32 cm thick porous PTFE sheet using a custom-built stainless steel tool comprised of two concentric stainless steel hollow rods with sharpened edges (o.d. 0.72 cm, i.d. 0.46 cm). All components were precision machined to form a water-tight seal.
Figure II.1. (Top panel) Components of the porous Teflon ring|Au disk electrode probe, A. (Middle panel) Cross section of the assembled probe, where \(a = 0.5\) cm, \(b = 0.7\) cm, \(c = 0.18\) cm, \(d = 0.3\) cm. (Lower panel) Schematic diagram of the electrochemical cell for online mass spectrometric measurements under forced convection generated by a jet impinging electrode: (A) porous Teflon ring|Au disk probe, (B) auxiliary electrode, (C) reference electrode, (D) jet nozzle, (E) bubbler, (F) Teflon lid, (G) glass cell.
Online mass spectrometric measurements were performed by immersing the ring-disk probe into ~400 mL of electrolyte solution (*vide infra*) in an ~500 mL cell (see lower panel, Figure II.1) with the electrode facing down directly in front of the tip of a nozzle (i.d. 1.52 and o.d. 1.91 mm) aligned along an axis normal to the flat surface of the probe. Adjustments were made to position the nozzle pointing to the center of the Au disk about 4 mm from its surface. About 400 mL of electrolyte solution was forced to flow through a u-type tubing manifold ending in the immersed nozzle using a valveless piston pump (FMI) (see Figure II.1). During operation, the column of liquid emerging from the nozzle impinged on the electrode and then spread radially along the surface of the probe bringing dissolved gaseous species in contact with the Teflon membrane. The actual volume of electrolyte in the cell at any given time was of about 300 mL. The flow rate was calibrated prior to the actual experiments by measuring the volume of the solution delivered per unit time. A Au foil (2.5 cm²) and a standard hydrogen electrode (SHE) were used as auxiliary and reference electrodes, respectively. The first step in the assembly of the ring-disk probe involves wrapping the Teflon membrane around the porous PTFE annulus followed by insertion of the Au electrode into the hollow section of the annulus. The latter is then pressed into a cavity in the solid PTFE holder (middle panel, Figure II.1) making sure the front surface of the disk as well as that of the Teflon supported membrane and the PTFE annulus lie on a single common plane as required for achieving a well-defined hydrodynamic flow. It should be stressed that the use of a Teflon membrane was found to be essential, as no gases could be detected using only
the porous plug under otherwise identical conditions. As shown in the figure, the back of the Au electrode is also pressed fit into a ledge made in the PTFE hollow cylinder. Gases present in the solution adjacent to the annulus surface permeate through the Teflon membrane and the porous Teflon annulus reaching a small void space adjacent to the wall of the Au cylinder and diffuse through two holes drilled on the ledge parallel to the main axis of the cylinder connected in turn to the mass spectrometer chamber. Contact to the working electrode was made by means of a spring as shown in the middle panel, Figure II.1.

The mass-spectrometer employed for these studies was a Dycor Quadlink Q100 M (Ametek) with Dycor 2000 software. The small chamber that housed the mass spectrometer was evacuated using a Leybold Turbovac 50 turbomolecular pump backed by a Leybold Trivac roughing pump. During the measurements the pressure inside the vacuum system was of about $2 \times 10^{-5}$ Torr. The $N_2$ signal ($m/z = 28$), $i(N_2^+)$, was collected with a dwell time of 15 ms and the data was acquired at a rate of ~11 points/s.

Experiments were performed in deaerated (Ar purged) hydrazine (monohydrate, Sigma-Aldrich, reagent grade, 100.4%) solutions in the range 0.2 to 1 mM in 0.1 M phosphate buffer (PB, pH 7) prepared from monosodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, Ultrapure, J. T. Baker, 99.9%) and disodium phosphoric acid ($\text{Na}_2\text{HPO}_4$, Ultrapure, J. T. Baker, 99.7%) and ultrapure water (18.3 MΩcm, EASYpureUV system, Barnstead) at room temperature. Potential control was achieved with a Pine potentiostat (RDE4)
which was in turn connected via a data acquisition card (National Instruments, USB-6009) to a personal computer. Data were collected at a rate of 1000 points/s and stored as the adjacent average of 250 points/s referred to hereafter as the raw data.

RESULTS AND DISCUSSION

Shown in panel A, Figure II.2 are the best-fit polarization curves obtained for the Au disk of the probe recorded at a rate of 5 mV/s, while flowing a 0.1 M PB (pH 7) containing hydrazine (N$_2$H$_4$) at different concentrations, i.e., 0.2 (cyan), 0.4 (blue), 0.6 (green), 0.8 (red), and 1.0 mM (black), at a rate $v_f = 0.081 \text{ cm}^3/\text{s}$, through the nozzle toward the center of the Au disk. For clarity, only scans toward negative potentials are displayed. The scattered points represent the raw current for data collected in the 0.2 mM N$_2$H$_4$ solution in PB, where the large amplitude oscillations are induced by the modulation in the flow rate introduced by the valveless piston pump. The latter was clearly evidenced in the Fourier transform of the data, which was characterized by a prominent sharp peak at precisely the same frequency as that of the rotor in the pump, i.e., 0.38 Hz (see Figure A2.1, Appendix 2).
Figure II.2. (A) Best-fit polarization curves collected with a Au disk (0.196 cm$^2$) at a rate of 5 mV/s, while flowing a 0.1 M PB (pH 7) containing hydrazine (N$_2$H$_4$) at different concentrations, i.e., 0.2 (cyan), 0.4 (blue), 0.6 (green), 0.8 (red), and 1.0 mM (black), at a rate $v_f = 0.081$ cm$^3$/s. For clarity, only scans toward negative potentials are displayed. The jagged line represents the raw current for data collected in the 0.2 mM N$_2$H$_4$ solution in PB. (B) Best fit $i(N_2^+)$ vs $E$ curve acquired simultaneously with curves in panel A.

A plot of the limiting current, $i_{lim}$, as a function of [N$_2$H$_4$] yielded a straight line with a very small negative intercept (see open symbols in panel A of Figure II.3). Also shown in this panel are data collected at three other values of $v_f$ (see solid symbols). It may thus be surmised that within the experimental conditions selected, the oxidation of N$_2$H$_4$ is first order in the reactant and that $i_{lim}$ is strictly diffusion controlled. This behavior is in agreement with that reported by Yan et al.,(17) who obtained linear $i_{lim}$ vs [N$_2$H$_4$] plots using a rotating (non-gas) porous Au electrode supported on glassy carbon in 0.1 M phosphate buffer (pH 8.5) for [N$_2$H$_4$] in the range 0.1–10 µM.
Figure II.3. (A) Plots of Au disk limiting currents as a function of $[\text{N}_2\text{H}_4]$ for four different flow rates $0.048$ (a), $0.081$ (b), $0.112$ (c), and $0.143$ (d) cm$^3$/s. The best linear fits to the data are as follows: (a) slope $S = 2.29 \times 10^{-4}$, intercept, $I = -1.02 \times 10^{-5}$; (b) $S = 3.05 \times 10^{-4}$, $I = -1.64 \times 10^{-4}$; (c) $S = 3.84 \times 10^{-4}$, $I = -2.35 \times 10^{-4}$; (d) $S = 4.43 \times 10^{-4}$, $I = -2.55 \times 10^{-5}$. $R^2 > 0.997$ for all four sets of data. (B) Plot of the limiting ion current as a function of $[\text{N}_2\text{H}_4]$ recorded at $\nu_f = 0.081$ cm$^3$/s. $S = 12.46 \text{mM}^{-1}$; $I = 0.697$; $R^2 = 0.988$.

The expression for $i_{\text{lim}}$ for a jet impinging electrolyte in the wall jet configuration is given by (18)

$$i_{\text{lim}} = (1.60k)nFC^\circ D^{2/3}\nu^{-5/12}\nu_f^{3/4}a^{-1/2}R^{3/4}$$

(II.1)

where $k$ is a constant, $n$, the number of electrons transferred, $F$, Faraday’s constant, $C^\circ$ and $D$, the bulk concentration and the diffusion coefficient of the electroactive species respectively, $\nu$, the kinematic viscosity, $\nu_f$, the flow rate, $a$, the nozzle diameter, and $R$, the radius of the disk electrode. The value of $D$ for $\text{N}_2\text{H}_4$, assuming $\nu = 0.0101$ cm$^2$/$\text{s}$, was determined from data collected from polarization curves recorded with a Au rotating disk electrode as a function of $\rho_{\text{N}_2\text{H}_4}$. 

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rotation speed for \([\text{N}_2\text{H}_4]\) = 0.2 mM (see Figure A2.2 in Appendix 2), yielding a value of \(1.33 \times 10^{-5} \text{ cm}^2/\text{s}\), which is in excellent agreement with that published in the literature.(17, 19) The general validity of eq II1 was assessed by calculating \(k\) based on the entire set of experimental data, yielding an average value of 0.868 ± 0.032. This value compares very well with that reported by Yamada and Matsuda, i.e., 0.86,(18) which provides strong evidence for the reliability of the hydrodynamic characteristics of the device.

Corresponding best fits to \(i(\text{N}_2^+)\) vs the applied potential \(E\) acquired simultaneously (see panel B, Figure II.2) displayed the same overall trend as the polarization curves, including clearly defined limiting values in the positive potential range. Also shown in this panel is the raw data for 0.6 mM \(\text{N}_2\text{H}_4\) (see scattered points). It is thus of interest from an analytical viewpoint to establish whether \(i(\text{N}_2^+)\) is proportional to the amount of \(\text{N}_2\) generated at the disk using the data in Figure II.2. To this end, the two signals were normalized to their corresponding limiting values. However, for this and all other concentrations examined, the plots of the best fits values for the normalized \(i(\text{N}_2^+)\) do not overlap their normalized current counterparts, as illustrated in Figure II.4 for \([\text{N}_2\text{H}_4]\) = 0.8 mM, clearly indicating the two signals are not proportional in the full potential range. This may not be surprising as the porous Teflon ring does not behave as the solid ring of a conventional rotating ring disk electrode (RRDE), for which its potential is set to a value where the redox reaction proceeds under strict diffusion control. Specifically, the thickness of the diffusion boundary layer and thus the
concentration profile of the dissolved gas along the surface of the porous annulus is nonuniform. Under these conditions, a theoretical analysis of the \( i(N_2^+) \) curves, not as yet available, will be far more involved than for a conventional RRDE.

Rather unexpectedly, however, a plot of \( i(N_2^+) \) recorded at \( i_{\text{lim}} \) as a function of \([N_2H_4]\) (panel B, Figure II.3) for \( \nu_f = 0.081 \text{ cm}^3/\text{s} \), was nevertheless found to be fairly linear.

*Figure II.4.* Normalized best fit dynamic polarization (blue) and \( i(N_2^+) \) vs \( E \) curves based on data recorded simultaneously in a 0.8 mM \( N_2H_4 \) in PB (pH 7) solution at \( \nu_f = 0.081 \text{ cm}^3/\text{s} \).
Two additional observations point to the complexities associated with this system: (i) The average $i(N_2^+)$ (see black symbols, left ordinate, Figure II.5) increased with flow rate, attained a maximum at $v_f \sim 0.08 \text{ cm}^3/\text{s}$, and decreased slowly thereafter to reach a fairly constant value at higher $v_f$. This phenomenon is unrelated to the electrochemical response, as a plot of $i_{\lim}$ vs $v_f^{3/4}$ (see insert in this figure), based on the values of $i_{\lim}$ as a function of $v_f$ recorded simultaneously (see blue symbols, right ordinate in Figure II.5) was linear, as predicted by eq II.1. (ii) Significant deviations from the linear behavior were reported by Wang et al. for measurements of the ion currents in aqueous solutions saturated with carbon dioxide and argon upon increasing the flow rate. (11) More specifically, the response of the mass spectrometer was smaller than that extrapolated from the lower flow rates as would be expected for mass transport hindrances through the membrane and/or porous plug.
Figure II.5. Plot of $i(N_2^+)$ as a function of the flow rate, $v_f$, recorded in a solution 0.6 mM $N_2H_4$ in 0.1 M PB (pH 7). Insert. Plot of $i_{\text{lim}}$ vs $v_f^{3/4}$ based on data collected simultaneously (see text for details).

CONCLUDING REMARKS

The porous Teflon ring|Au disk electrode assembly described in this letter made it possible to conduct online mass spectrometric measurements under well-defined forced convection conditions generated by a jet impinging electrolyte using the oxidation of $N_2H_4$ on Au in an aqueous buffered electrolyte (pH 7) as a model system. Both the current and the mass spectrometric response, $i(N_2^+)$, as a function of the applied potential were sigmoidal, reaching limiting values at
sufficiently high overpotentials, which showed a linear dependence with \([\text{N}_2\text{H}_4]\).

Plots of \(i(N_2^+)\) as a function of the flow rate, however, displayed a peak followed by a flat plateau at higher \(v_f\). This phenomenon was attributed to mass transport hindrances through the Teflon membrane and/or porous Teflon plug. A theoretical analysis of this system is currently being pursued and will be reported in due course.

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Appendix 1

I. X-Ray Diffraction Results

Figure A1.1. Transmission- and reflection-mode X-ray diffraction profiles for various polar polyimides containing 1 or 3 nitrile groups.
II. Details of Calculation

II.1. Repeating Unit Density ($m^3$)

\[ N = \frac{\rho}{M_{RU}} N_A \], where $\rho$ is density of the polymer, $M_{RU}$ is the molar mass of a repeating unit and $N_A$ is the Avogadro’s number.

II.2. Repeating Unit Dipole Moment ($D$)

\[ \mu_{RU} = \mu_{DA} - \mu_{DAm} \], where $\mu_{DA}$ is the dipole moment of the dianhydride part and $\mu_{DAm}$ is the dipole moment of the diamine part of the polyimide. The two dipole moments are subtracted because they are assumed to point in the opposite directions.

II.3. Predicted Dipolar Polarization ($C/m^2$)

\[ P_{dip} = N \mu_{RU} \left( \coth u - \frac{1}{u} \right) \], here $u = \frac{\mu_{RU} E}{k_B T}$, where $N$ is the repeating unit density, $\mu_{RU}$ the dipole moment of a repeating unit, $E$ the applied electric field (100 MV/m for all samples), $k_B$ the Boltzmann constant, and $T$ the absolute temperature (463.15 K). The function in the parenthesis is also known as the Langevin function.
II.4. Polarization Only Due to Dipolar Motion

\[ P_{\text{dip}} = P_{\text{DE}} - P_{\text{BDS}} = P_{\text{DE}} - (\varepsilon_{\text{BDS}} - 1)\varepsilon_0 E, \]

where \( P_{\text{DE}} \) is the polarization from a \( D-E \) loop measured at 100 MV/m, 190 °C, and 1 kHz, and \( P_{\text{BDS}} \) is the polarization calculated from the permittivity \( \varepsilon_{\text{BDS}} \) measured with broadband dielectric spectroscopy at -150 °C, 100 kHz, and under an applied voltage of 1 Vrms. \( \varepsilon_{\text{BDS}} \), since measured at a very low temperature and high frequency, is assumed to only contain contributions from electronic and vibrational polarizations. \( E \) is the electric field used in the \( D-E \) loop measurements and is equal to 100 MV/m.

II.5. Calculating Permittivity from Molar Refraction

From the Lorentz-Lorenz relation \( R_M = \frac{\varepsilon_{\text{e},e} - 1}{\varepsilon_{\text{e},e} + 2} \frac{M_{\text{RU}}}{\rho} \), we can express \( \varepsilon_{r,e} \) from electronic polarization as:

\[ \varepsilon_{r,e} = \frac{2R_M\rho + M_{\text{RU}}}{M_{\text{RU}} - R_M\rho}, \]

where \( R_M \) is the molar refraction of the repeating unit. The molar refraction values are obtained by adding up the refractions of bonds that make up the repeating unit. The bond refraction values are obtained from literature. To account for the vibrational polarization, which is approximately 20% of that of the electronic polarization, the \( R_M \) value in the above equation will be multiplied by 1.2 in order to obtain the \( \varepsilon_r \) from both electronic and vibrational polarizations.
Figure A2.1. Fourier transform of the current measured at a potential of 1.0 vs SHE while a solution 0.6 mM hydrazine in 0.1 M phosphate buffer (pH 7) was impinging on the electrode at a flow rate of 0.018 cm$^3$/s.
Figure A2.2. Polarization curves recorded with the Au disc of an Au-Au RRDE in 0.1 M PBS (pH 7) containing 0.2 mM hydrazine at different rotation speeds as indicated. Insert: Plot of $i_{\text{lim}}$ as a function of $\omega^{1/2}$. Linear Fit: Slope: 0.01869 \pm 1.42032 \times 10^{-4}$; Intercept: -0.01237 \pm 0.00471


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