Electrical Impedance Analysis of Carbon Nanotube-Polyelectrolyte Thin Film Strain Sensors

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Abstract
Single wall carbon nanotubes (SWNT) are an impressive material at the center of the nanotechnology revolution; in particular, SWNT posses a unique array of physical properties including high stiffness and good chemical reactivity. SWNTs are explored for inclusion in polymer matrices to produce thin films with electrical properties that exhibit sensitivity to strain loading. A layer-by-layer (LbL) fabrication procedure is detailed for the manufacture of free-standing thin films defined by interdigitated phase homogeneity and high strength. A characteristic feature of the proposed SWNT-polyelectrolyte (SWNT-PE) thin films is that nano-scale constituents can be deliberately varied to attain desired macroscopic electromechanical properties. Concentrations of SWNT and PE are varied to yield thin film strain sensors with high gage factors. SWNT-PE thin film strain sensors are patterned upon substrates as inductive coil antennas that can be wirelessly interrogated by a remote wireless reader. To fully characterize the wireless read-out mechanism of the patterned SWNT-PE antennas, electrical impedance spectroscopic (EIS) analysis of the thin films is performed.

Keywords: Nanotechnology, carbon nanotubes, strain sensors, structural health monitoring

1. Introduction
Nanotechnology has emerged as a promising technology that offers an unprecedented opportunity to design materials at the molecular level. One fundamental building block of the nanotechnology field is the carbon nanotube. The carbon nanotube was first discovered by Iijima (1991) and consists of carbon atoms bonded in a helical crystalline structure. Carbon nanotubes can be manufactured in multiple forms including single-wall (SWNT) and multi-wall (MWNT) nanotubes. SWNT are defined geometrically by one cylindrical lattice of carbon atoms (Figure 1) while MWNT are comprised of multiple helical lattices concentrically positioned. SWNT have diameters ranging from 0.7 to 10 nm and can be grown to long lengths offering aspect ratios as large as 103 (Saito et al., 1998). Carbon nanotubes posses a unique set of physical properties that heighten interest in their use. For example, SWNT have incredible stiffness with an elastic modulus experimentally verified to be greater than 1000 GPa (Treacy et al., 1996). Electrically, SWNT can exhibit conductivity properties consistent with conductors and semi-conductors depending upon the orientation of the carbon atoms in the tube’s lattice structure. In recent years, a plethora of work has been published regarding the chemical modification of carbon nanotubes (termed functionalization) to render their use in a broad array of chemical processes and applications (Lin et al., 2003).

A new generation of smart structure technologies (specifically, sensors and actuators) can be designed by adopting the “bottom-up” approach offered by the tools and processes associated with the nanotechnology field. Within the smart structures and structural health monitoring communities, a number of researchers have begun to explore the adoption of nanotechnology as a means of designing sensing materials that exhibit measurable changes in their electrical properties due to mechanical and chemical stimuli. Dharap et al. (2004) report on the use of homogenous SWNT films formed by vacuum filtration of SWNT solutions as strain sensors. The SWNT film, commonly referred to as buckypaper, exhibits linear changes in conductivity when mechanically strained to levels as large as 400 μm/μ. One limitation of buckypaper is the weak van der Waals attraction between individual SWNT resulting in the brittle failure of the film at low strains. Kang et al. (2006) propose reinforcing SWNT with a polymer matrix to provide a SWNT-based strain sensor with improved strain capacity. Their method first disperses SWNT in solution using dimethyl formamide (DMF) solvent and a polymer binding agent (polymethyl methacrylate) before casting in a mold. The result is a strain sensor exhibiting a linear
change in resistance as a function of strain to levels as high as 1500 µm/m. Alternatively, a layer-by-layer (LbL) fabrication method is proposed for the manufacture of a SWNT-polymer composite materials intended for strain sensing (Loh et al., 2005). The LBL method produces piezoresistive thin films with highly homogenous morphologies that are capable of high strain in excess of 10,000 µm/m (Mamedov et al., 2002, Loh et al., 2006a).

There are many advantages associated with designing carbon nanotube-polyelectrolyte composite materials at the atomistic length-scale for use as strain sensors. Principle among these advantages is the ability to deposit the conformable thin film upon any structural surface (e.g. flat, curved, irregular) and in any shape desired. As a result, SWNT-PE thin films can be deposited to form passive wireless sensors that operate along the same principles as radio frequency identification (RFID) technologies (Paret, 2005). Specifically, the SWNT-PE thin film can be patterned into coil antenna shapes that can communicate with a remote reader without the need for a native power source (e.g. batteries). The convenience offered by this elegant readout mechanism is underscored by the recent emergence of wireless sensors as viable substitutes to traditional tethered structural monitoring sensors (Lynch and Loh, 2006). The conceptual design of an RFID sensor is quite simple with a resistor, capacitor (for received power storage), and inductor (for electromagnetic coupling with the interrogator) placed in a parallel circuit (Figure 2a). A remote reader consists of an alternating current (AC) supply and an inductive antenna; the AC current passing through the antenna produces an alternating magnetic flux field in the vicinity of the antenna. When an RFID sensor with its own inductive antenna is placed in close proximity to the alternating magnetic field generated by the reader, the sensor will generate its own alternating current due to the magnetic field. This electromagnetic coupling allows the remote reader to sense changes in the impedance of the coupled RFID sensor tag. For example, changes in the resistance and/or capacitance of the RFID sensor can be detected by the remote reader. Loh et al. (2006b) illustrate that SWNT-PE thin films exhibit electrical properties identical to an RC-parallel circuit. Combined with an SWNT-PE thin film patterned as an inductive coil antenna, an RFID sensor can be constructed (Figure 2b). When the SWNT-PE thin film is strained, changes in the film conductivity results in changes in the RFID sensor impedance that can be measured by a remote reader (Loh et al., 2006b).

Before an RFID sensor can be fabricated from SWNT-PE composites, the electrical impedance properties of the material must first be accurately assessed. After the resistance and capacitance of SWNT-PE thin films are quantified as a function of alternating current frequency, these impedance properties can be used to analytically model and optimize the design of RFID sensors fabricated from SWNT-PE thin films. In this study, the electrical impedance properties of the SWNT-PE thin films are illuminated through electrical impedance spectroscopy (EIS). An EIS analysis is conducted upon an unloaded SWNT-PE thin film to first characterize its impedance response. This response is used to formulate an equivalent electrical circuit that captures the frequency dependent electrical response of the SWNT-PE bulk material when an alternating current is applied. Next, the SWNT-PE thin films are cyclically loaded with EIS analyses conducted during loading. Changes in the thin film conductivity as a function of strain are illuminated and incorporated in the equivalent electrical circuit model. The paper concludes with a discussion on the proposed SWNT-PE thin film RFID sensor designed for strain sensing.

2. Fabrication of Conformable Carbon Nanotube Composite Films

While individual carbon nanotubes are endowed with impressive mechanical, electrical, and thermal properties, their hydrophobic nature and tendency to clump in solution has presented many fabrication challenges that limit the workability of the material. To date, many researchers have utilized the “brute-force” method of vacuumfiltrating aqueous solutions of carbon nanotubes to form thin carbon nanotube mats on filtration paper, commonly termed buckypaper. However, the material is brittle and fragile due to the weak van der Waals and electrostatic forces between nanotubes that hold the buckypaper together. In response to this limitation, polymer-carbon nanotube composites have been proposed. Unfortunately, most reported composites have only shown moderate strength enhancements when compared to other carbon fiber composite materials. A cause for the lack of impressive strength enhancement has been
attributed to phase segregation in the final composite. To fully harness the mechanical properties offered by carbon nanotubes, uniformly distributed nanotube connectivity throughout a polymer matrix is essential.

Alternative to the brute-force methodology for the fabrication of SWNT buckypaper, a homogeneous thin film of controlled thickness and macro-scale properties can be achieved using a layer-by-layer process as illustrated in Figure 3 (Decher 1997, Kotov 2001, and Paloniemi et al., 2006). This low cost, template assisted self-assembly process entails the sequential deposition of oppositely charged polyanions and polycations for multilayer film fabrication. Each additional monolayer adsorbs onto its previous monolayer due to van der Waals forces, electrostatic force, and hydrogen bonding. The superiority of the LbL technique stems from its fundamental solution-based multicomposite thin film fabrication principle to allow for the incorporation of a wide range of materials.

In this project, SWNT-PE multilayer composites of controlled morphologies are fabricated with the LbL technique. Preparation of the polyanion and polycation solutions begins by dispersing SWNTs (from Carbon Nanotechnologies, Inc.) in a 1.0% by wt. high molecular weight ($M_c$) poly(sodium 4-styrene-sulfonate) (PSS, 1,000,000 $M_c$, Alrich) solution. Steric stabilization can be achieved by subjecting SWNTs in PSS to 180 min of sonication (135W, 42 kHz) followed by 90 min at 30% amplitude of high-powered tip deep sonication (3.178 mm tip, 500 W, 22.0 kHz). The PSS dispersive agent noncovalently bonds to the surface of the SWNT and departs an overall negative charge to the aqueous SWNT-PSS solution. On the other hand, a 1.0% by wt. poly(vinyl alcohol) (PVA, Sigma) solution is employed as the LbL counterpart.

The LbL method begins by dipping a charged glass substrate treated with Piranha solution (3:7 H$_2$O$_2$:H$_2$SO$_4$) in the polyelectrolyte solution (PVA) for 5 min. After a PVA monolayer is deposited, the substrate is rinsed in 18 MOhm deionized water for 3 min and dried for 15 min for stronger adhesion to the substrate. Deposition of the second monolayer continues by dipping the substrate in the suspended SWNT-PSS solution for 5 min and subsequently washing (3 min) and drying (15 min). This cycle completes the fabrication of one (SWNT-PSS/PVA) bilayer, and the process is repeated to fabricate films of 50 or 100 bilayers.

3. Electromechanical Characterization of Thin Films

3.1. EIS Background

In a previous study, an equivalent circuit model has been devised to describe SWNT-PSS/PVA thin films loaded in tensile-compressive cyclic strain (Loh et al., 2006a). The time-domain analyses between numerically calculated equivalent circuit responses and experimental bulk film changes in resistance to strain (measured with an Agilent 34401a Multimeter) show considerable agreement. The simulated equivalent circuit response (calculated bulk film resistance) is calculated based on a constant direct current (DC) current supply from the Agilent Multimeter. However, for RFID transponder tags, its response to a local magnetic field induces an alternating current (AC) at various frequencies. A new approach is therefore needed to characterize the electrical properties of SWNT-PSS/PVA thin films as a function of signal frequency. Electrical impedance spectroscopy is employed to derive an AC circuit model and to investigate SWNT-PSS/PVA thin film responses to strain loading.

Electrical impedance spectroscopy is a frequency-domain analysis that characterizes the electrical properties of materials and their interfaces using electronically conducting electrodes (Barsoukov and Macdonald, 2005). Electrical measurements are taken by applying a monochromatic AC electrical stimulus of known voltage ($V(t) = V_0 \sin(\omega t)$) and frequency ($f = \omega / 2\pi$) and measuring the subsequent steady-state current response from the system ($I(t) = I_0 \sin(\omega t + \theta)$ where $\theta$ is the phase difference between voltage and current). While a time-domain analysis can extract material behavior due to an AC stimulus, the relation between input stimulus and output response is typically very complex requiring
differential equations. On the other hand, impedance measurements (by definition a complex quantity denoted as \(Z(\omega) = Z' + jZ''\)), inherently take the phase difference and attenuation between input and output into account. In rectangular coordinates, the components of impedance, \(Z(\omega)\), can be expressed as:

\[
\begin{align*}
\text{Re}(Z) &= Z' = |Z| \cos(\theta) \\
\text{Im}(Z) &= Z'' = |Z| \sin(\theta)
\end{align*}
\]

(1a) (1b)

EIS analyses performed on SWNT-PSS/PVA thin films are conducted by employing a Solartron 1260 impedance/gain phase analyzer. Equipment such as the Solartron 1260 can be classified as an automated frequency response analyzer that can directly measure impedance by correlating the cell response \(S(t)\) as shown in equation 2) with two synchronous reference signals. One reference signal (\(\sin \omega t\)) is in phase with the applied AC perturbation \(P(t)\) as shown in equation 2) while the other is 90° out-of-phase (\(\cos \omega t\)) (Barsoukov and Macdonald, 2005).

\[P(t) = P_0 \sin(\omega t)\]

(2)

The thin film under investigation exhibits an electrical response, \(S(t)\), to the perturbation signal that is governed by its impedance \(Z(\omega)\).

\[S(t) = P_0|Z(\omega)| \sin(\omega t + \phi(\omega)) + \sum_{n} A_n \sin(n \omega t - \phi_n) + N(t)\]

(3)

The first term in the cell response \(S(t)\) contains the fundamental component of the transfer function of the thin film:

\[|Z(\omega)| e^{\phi(\omega)}\]

(4)

The subsequent second and third terms in equation 3 represents harmonics and noise of the cell response, respectively. From the known input AC stimulus and the resulting cell response, the real and imaginary impedance components can be directly calculated by the automated frequency response analyzer.

3.2. EIS Response of SWNT-PSS/PVA Thin Films

Using the Solartron 1260 impedance/gain phase analyzer coupled with a four-probe measurement technique to minimize stray capacitance due to lead wires, the EIS response of various SWNT-PSS/PVA thin films is measured. Particularly, films fabricated with different LbL fabrication parameters and thicknesses have been characterized through EIS analysis. The response of SWNT-PSS/PVA multilayer films to AC stimuli of varied frequencies yields a semicircular shape in the complex impedance plane plot, widely known as the Cole-Cole plot (Figure 4a). The semi-circular Cole-Cole response suggests an RC-circuit behavior, thus confirming the previously proposed circuit model (Loh et al., 2006a). More interestingly, for 100 layer thick thin films defined by a high concentration (0.8 mg/mL) of SWNT in 1.0% by wt. PSS solution, two semi-circles appear (Figure 4b); the addition of the second semicircle implies a different mode of electronic conduction at increasing AC frequencies (a two phase process). For all SWNT-PSS/PVA thin films, the dominant larger semicircle may result from electron conduction through the SWNT-PSS interface (higher resistance), whereas the additional semicircle may be caused by electron flow through individual SWNTs in the polymer matrix (lower resistance due to ballistic transport-type behavior of individual SWNTs).

From preliminary results of EIS characterization of SWNT-PSS/PVA thin films, it has been verified that the previously proposed circuit model from a time-domain DC stimuli analysis is similar (Loh et al., 2006a); an updated model that captures the thin film AC behavior is devised from EIS analytical results as shown in Figure 5. Previously, it was assumed that only one resistor \(R_f\) was time-variant, such that its resistance exponentially decayed over time due to a hypothesized DC current induced thermal-chemical process. Upon investigation of the thin film response from a frequency-domain perspective, it is observed that the equivalent circuit capacitor \(C_f\) also exponentially decays in magnitude over time. While the decay of \(R_f\) is irreversible due to a chemical combination at nanotube-to-nanotube junctions, the exponential decay of \(C_f\) is completely reversible upon removal of the AC stimulus. The reason for this reversible decay in film capacitance may be due to increased probability of electron tunneling between SWNTs in the polymer matrix over time. Electron tunneling allows greater charge movement, thus reducing the overall resistance and capacitance of the thin film. In fact, this process cannot be easily isolated through a time-domain DC analyses as previous studies have done. Hence, the advantage of electrical impedance spectroscopy is that one can investigate the frequency dependence of unknown systems to identify a unique equivalent AC circuit model to fully describe the electrical properties of a material under investigation.
Table 1. Fabricated SWNT-PSS/PVA Thin Films for EIS Characterization

<table>
<thead>
<tr>
<th></th>
<th>0.25 mg/mL SWNT</th>
<th>0.50 mg/mL SWNT</th>
<th>0.80 mg/mL SWNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 bilayers</td>
<td>0.4%, 0.7%, 1.0% PSS</td>
<td>0.4%, 0.7%, 1.0% PSS</td>
<td>0.4%, 0.7%, 1.0% PSS</td>
</tr>
<tr>
<td>100 bilayers</td>
<td>0.4%, 0.7%, 1.0% PSS</td>
<td>0.4%, 0.7%, 1.0% PSS</td>
<td>0.4%, 0.7%, 1.0% PSS</td>
</tr>
</tbody>
</table>

3.3. EIS Characterization of Unstrained SWNT-PSS/PVA Thin Films

As mentioned earlier, the three primary constituents of passive, wireless RFID transponder tags includes a resistor ($R$), a capacitor ($C$), and an inductor ($L$) oriented in a parallel RLC-circuit (Figure 2a). Current RFID transponder technology utilizes discrete circuit elements or micro-machined parts on silicon substrates for its resistor and capacitor connected to a coil antenna (inductor). While micro-machined resistors and capacitors significantly reduce the form factor of the transponder, further reduction in cost and size could by adopting thin film circuit elements (resistor, capacitor, inductive coil). LbL fabrication parameters can be varied to yield films of specific resistance and capacitance. In particular, three LbL fabrication parameters (SWNT concentration, PSS concentration, and film thickness) have been identified as parameters that impact macro-scale film properties. First, by increasing SWNT concentration during layer-by-layer assembly, greater nanotube deposition can be achieved to increase overall conductivity of the film. Second, while increasing PSS concentration improves SWNT suspension for greater SWNT film deposition, the higher concentrations of PSS simultaneously causes higher polyelectrolyte deposition. Finally, with each additional layer of SWNT deposited, bulk-film resistivity should decrease due to increased presence of carbon nanotubes. Thus, by varying LbL fabrication parameters, a SWNT-PSS/PVA thin film can be fabricated with specific $R$ and $C$ parameters which inherently behave as an RC-parallel circuit. The addition of an inductor to form a wireless RFID transponder tag can be accomplished by connecting a coil antenna (also patterned from the SWNT-PSS/PVA thin film) of a certain inductance ($L$).

To uncover the relationship between the three LbL fabrication parameters of interest and the corresponding bulk film properties, a total of 18 films are fabricated for EIS characterization (Table 1). Electrical impedance spectroscopy is conducted for all 18 films, and the resulting experimental data is fitted with an updated equivalent circuit model (including the effect of capacitance decay as shown in Figure 5) using a model updating algorithm to minimize the sum of least-squares difference between experimental and numerical data points. In particular, seven parameters are fitted simultaneously to describe the unstrained behavior of SWNT-PSS/PVA thin films subjected to AC stimuli of a range of frequencies (25 kHz – 150 kHz). The model fitting parameters include: (1) $R_i$ the thermal-chemical and strain sensitive resistor; (2) $R_{st}$ the resistor in parallel; (3) $C_{st}$ the capacitance in parallel; (4) and (5) A and B to model the...
The real and imaginary components of the complex impedance can be separated to calculate the total least-squares difference between experimental and numerical data. Figure 6 presents a representative model fitting of numerically calculated EIS values to experimental data; results reveal good agreement between the two, thus validating the proposed circuit model (Figure 5). Upon validation of the equivalent parallel-RC circuit model, the model updating algorithm (simulated annealing) is carried out for all 18 thin film specimens to identify any trends, if any, in the discrete circuit parameters as a function of different LbL fabrication parameters. The results for fitted $R_i$ and $R_{st}$ values are tabulated in Table 2 and 3, respectively.

In general, the model-fitted values for $R_i$ and $R_{st}$ follow well-defined trends. First, as carbon nanotube concentration is increased from 0.25 mg/mL to 0.80 mg/mL, a progressive decrease in $R_i$ and $R_{st}$ is observed due to the increase in the deposition of carbon nanotubes. On the other hand, as PSS concentration is increased, although greater SWNT suspension have been verified (Loh et al., 2006a), the deposition of finely dispersed SWNT is masked by the excessive thermal-chemical resistivity exponential decay of $R_i$, ($R_i = R_i + A e^{Bt}$); (6) and (7) $G$ and $H$ to model exponential decay of $C_{st}$ due to increased probability of electron tunneling between neighboring nanotubes ($C = C_{st} - G e^{Ht}$). The total impedance of the RC-parallel circuit at a particular frequency, $\omega$, can be calculated:

$$Z_{eq}(\omega) = R_i + A e^{Bt} + \frac{1}{\sqrt{R_{st}^2 + i\omega (C_{st} - G e^{Ht})}}$$  

(6)

The real and imaginary components of the complex impedance are tabulated in Table 2 and 3, respectively.
Table 3. Model updated equivalent circuit model fitted $R_i$ values (Ohms).

<table>
<thead>
<tr>
<th>SWNT Concentration</th>
<th>0.25 mg/mL SWNT</th>
<th>0.50 mg/mL SWNT</th>
<th>0.80 mg/mL SWNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4% PSS 50 bilayers</td>
<td>5196.0</td>
<td>5703.8</td>
<td>4084.8</td>
</tr>
<tr>
<td>0.4% PSS 100 bilayers</td>
<td>2680.0</td>
<td>408.0</td>
<td>379.2</td>
</tr>
<tr>
<td>0.7% PSS 50 bilayers</td>
<td>28078.7</td>
<td>7056.3</td>
<td>6645.6</td>
</tr>
<tr>
<td>0.7% PSS 100 bilayers</td>
<td>7641.7</td>
<td>2066.9</td>
<td>1492.0</td>
</tr>
<tr>
<td>1.0% PSS 50 bilayers</td>
<td>15462.7</td>
<td>38287.8</td>
<td>13012.1</td>
</tr>
<tr>
<td>1.0% PSS 100 bilayers</td>
<td>14394.0</td>
<td>5126.7</td>
<td>3334.3</td>
</tr>
</tbody>
</table>

deposition of PSS, thus producing the effect of increasing $R_i$ and $R_{st}$ with higher PSS concentrations. These trends are graphically displayed in Figures 7a and 7b. Furthermore, one can also observe the decrease in overall film resistance simply by increasing film thickness. This phenomena can be easily explained by assuming each layer acts as a resistor; each additional monolayer corresponds to the addition of a parallel resistor to the circuit thus reducing the total equivalent resistance of the film. Using the data derived from the electrical impedance analysis of unstrained SWNT-PSS/PVA thin films, one can begin to tailor specific film impedance properties. The ability to tailor thin film impedances is especially useful for applications such as RFID sensors where the designer might desire a specific resonant frequency of the wireless device.

4. Tuning of Nano-scale Properties for Strain Sensing

Earlier time-domain studies have shown that maximum gage factor (linear change in thin film resistance with strain) can be attained for the SWNT-PSS/PVA thin films as one increases carbon nanotube and PSS (dispersing agent) concentrations while reducing the number of layers (50 bilayers) (Loh et al., 2006a). In particular, (SWNT-PSS/PVA)$_{50}$ (where the subscript denotes the number of bilayers) thin films fabricated with 0.5 and 0.8 mg/mL SWNT in 1.0% by wt. PSS exhibits a gage factor between ~1.5 to ~1.9 as compared to a gage factor of 2.1 for typical metal-foil strain gages. While it is anticipated that by further increasing SWNT and PSS concentrations one can produce higher gage factors, it is hypothesized that the aforementioned 5 min LbL deposition time is insufficient; more carbon nanotubes can potentially be deposited by simply increasing substrate dipping time. With greater nanotube deposition, more nanotube-to-nanotube junctions are present for enhanced strain sensing (Stadermann et al., 2004).

Figure 7. (a) Strain and thermal-chemical sensitive resistor $R_i$ decreases resistance as carbon nanotube concentration is increased (a similar effect is observed for $R_{st}$) while PSS concentration is fixed; (b) Plot of $R_{st}$ for 100-bilayer films showing increasing resistance with greater PSS concentration (SWNT concentration fixed).
Investigation of optimizing dipping time for greatest nanotube deposition per dipping cycle is accomplished by utilizing UV-Vis absorption spectroscopy to indirectly measure the relative nanotube deposition in (SWNT-PSS/PVA)_{5} multilayer films fabricated with varied dipping times. UV-Vis absorption spectroscopy analytically measures the amount of light across a broad spectrum of wavelengths (300 – 900 nm) absorbed by a chemical substance (in this case SWNT) as UV light passes through the sample; greater absorbance implies greater nanotube deposition. Five-bilayer films fabricated with 1, 2, 5, 10, 15, 20, 25, and 30 min dipping times are subjected to UV-Vis, and their corresponding absorbance spectrum is captured. The UV-Vis absorbance data suggests that a 5-min dipping time in fact underutilizes the amount of material capable of being deposited during LbL fabrication. It can be seen that significantly higher nanotube deposition can be achieved by increasing the dipping time to 15 to 25 min (Figure 8). Consequently, (SWNT-PSS/PVA)_{50} films dipped for 20 min in SWNT-PSS and 1.0% by wt. PVA will be utilized to study how the impedance spectrum of the film changes with strain.

Sample preparation for strain testing begins by etching the thin film off one side of the glass substrate. The glass with film still on one side of the glass is cut into rectangular shapes of approximately 5 mm x 10 mm using a diamond tip scriber. The SWNT-PSS/PVA thin film on glass is then epoxy mounted (CN-Y post-yield epoxy, Tokyo Sokki Kenkyujo) to a 3.8 cm x 30.5 cm x 1.9 cm PVC bar. Electrical contacts for four-probe electrical impedance analyses are established using thin wire wrap and by drying silver paste (Ted Pella) across the film and leads. After sufficient drying, an MTS-810 load frame is employed to apply cyclic tensile-compressive loading up to ±5,000 µm/m strain to the film and specimen (Figure 9). The EIS response of the thin film is captured at every 2,500 µm/m strain by holding the specimen at that particular displacement. A total of nine EIS analyses are taken during the one-cycle tensile-compressive loading as shown in Figure 10. The corresponding Cole-Cole plots for each strain state are then overlaid in Figure 11. It can be observed that the thermal-chemical effect that affects $R_{i}$ induces a leftward shift of the entire Cole-Cole plot.

Although the thermal-chemical effect dominates the behavior of the thin film under strain, the well-behaved exponentially decaying model can be removed from the EIS raw data. Upon completion of testing, the SWNT-PSS/PVA frequency response is fitted with the proposed equivalent circuit model (Figure 5) using a model-updating algorithm. Upon identification of circuit parameters through model fitting, the fitted strain sensitive resistor values for each test (each strain state) can be plotted as shown in Figure 12. Using the unstrained states as control variables, an exponentially decaying model can be fitted to remove the thermal-chemical effect from $R_{i}$, leaving any change in resistance due to applied strain (Figure 13). The gage factor, $GF$, for this particular SWNT-PSS/PVA thin film can be determined:

$$GF = \frac{\Delta R_{i}}{R_{i}/\epsilon} = 0.66$$  

(7)

The gage factor determined is lower than anticipated (< 2.1) and is lower than gage factors calculated for the DC circuit models previously formulated in other studies (Loh et al., 2006a). One reason for the lower gage factor can be that higher
5. Conclusions

This paper has explored the use of electrical impedance spectroscopy (EIS) to characterize the electrical properties of SWNT-composite thin films subjected to AC electrical signals. The study is motivated by an ongoing research program that is exploring the patterning of SWNT-PSS/PVA thin films into RFID strain sensors. The EIS analyses allow for the quantification of the resistance and capacitance properties of the thin films as a function of the applied AC frequency. EIS has also be of great utility in identifying how these AC electrical properties change when mechanical strain is applied. The results suggest the resistance of the film is sensitive to strain with gage factors on the order of 0.6 encountered. Future work is needed to further identify the fabrication parameters of the LbL assembly method that can be optimized to attain higher gage factors as well as to remove the time-dependent drifts in resistance encountered in the thin films.
6. Acknowledgements

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7. References


