

High Efficiency Electrolyte Lithium Battery and RF Characterization

Wei Quan, Liu Chao, Mohammed N. Afsar

Abstract—The dielectric properties and ionic conductivity of novel "ceramic state" polymer electrolytes for high capacity lithium battery are characterized by Radio frequency and Microwave methods in two broad frequency ranges from 50 Hz to 20 KHz and 4 GHz to 40 GHz. This innovative solid polymer electrolyte which is highly ionic conductive (10^{-3} S/cm at room temperature) from -40°C to $+150^{\circ}\text{C}$ can be used in any battery application. Such polymer exhibits properties more like a ceramic rather than polymer. The various applied measurement methods produced accurate dielectric results for comprehensive analysis of electrochemical properties and ion transportation mechanism of this newly invented polymer electrolyte. Two techniques and instruments employing air gap measurement by Capacitance Bridge and in-waveguide measurement by vector network analyzer are applied to measure the complex dielectric spectra. The complex dielectric spectra are used to determine the complex alternating current electrical conductivity and thus the ionic conductivity.

Keywords—Polymer electrolyte, dielectric permittivity, lithium battery, ionic relaxation, microwave measurement.

I. INTRODUCTION

BATTERY face significant technical limitations relative to safety, cost, and energy density; improvement has been incremental in addressing these concerns. The electrolyte serves as a medium to transport the ions involved in the charging/discharging cycle of the cell. In addition, a separator has to isolate the anode from the cathode electronically. While ceramic or polymeric separators (which is also called as solid polymer electrolytes) have to be placed between the electrodes when liquid electrolytes are used, both functions ion conduction and separation can be realized in a single thin membrane when polymer electrolytes are used [1]. This innovative solid polymer electrolyte combines the properties of polymers, such as easy processability, design flexibility, light weight, shape versatility, safety and nontoxicity, with the electrical properties of ceramic electrolyte.

To characterize both the electronic conductivity and ionic conductivity is significant in the application of solid polymer electrolyte [2]. Usually, an AC impedance spectroscopy is employed with two inert blocking electrodes to clamp the polymer electrolyte [3]-[5].

In this paper, non-contact RF dielectric measurement is newly applied to this solid polymer electrolyte successfully over broad frequency range from 50 Hz to 40 GHz. The noncontact methods can avoid the electrode phenomena in

characterizing the electrolyte comparing with traditional contact clamping measurement [6], [7]. In the contact measurement, the electrodes clamp the polymer electrolyte as tight as possible. However, the real contact area is quite a small ratio to the electrode area which leads to a great uncertainty in the measurement. The non-contact measurement methods eliminate such uncertainty of contact area which causes errors in the calculated conductivity values.

A precise capacitance bridge Andeen-Hagerling 2700A Bridge with LD-3 dielectric capacitance cell and Agilent 8510C vector network analyzer with 8 different waveguides are employed to determine the complex permittivity spectra of the solid polymer electrolyte. Complex permittivity data were acquired from 50 Hz to 20 kHz by the Capacitance Bridge and 2 GHz to 40 GHz by the vector network analyzer. The complex permittivity spectra were then converted to complex impedance spectra and complex conductivity spectra. Ionic relaxations are observed and determined from the loss tangent spectra.

II. ELECTROLYTE ANALYZE

In this paper, the "ceramic state" polymer material has already shown the great potential in battery electrolyte applications. The polymer has very low electronic conductivity and pretty high ionic conductivity even at very low temperature. Therefore it is perfect to work as an electronic isolator and ionic conductor in a wide temperature range.

Conductivity measurements as a function of temperature vs. conventional polymer (PEO/TFSI) and traditional Celgard separator soaked with liquid electrolyte are shown in Fig. 1. It shows that the new "ceramic" polymer electrolyte performs totally different from the conventional polymer electrolyte while the temperature changes. The conductivity of conventional polymer increases as more and more polymer molecules turn into melted state as the temperature increases. The new "ceramic" polymer electrolyte has excellent ionic conductivity at room temperature and even better than liquid electrolyte at low temperatures. This demonstrates the "ceramic state" polymer electrolyte is perfect for battery applications.

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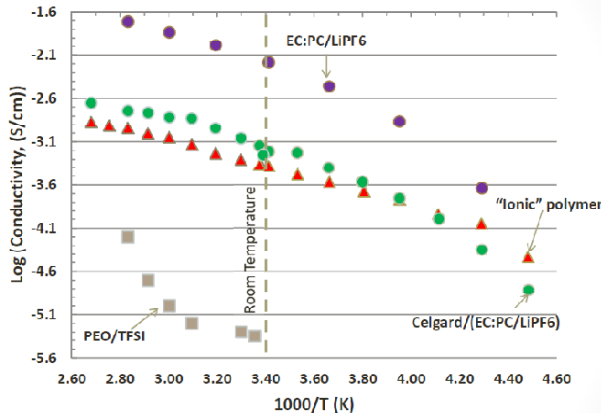


Fig. 1 “Ionic” (“ceramic state”) polymer conductivity is much higher than PEO/TFSI electrolyte and comparable to traditional Celgard separator soaked with liquid electrolyte at room temperature. At low temperatures “Ionic” electrolyte is superior

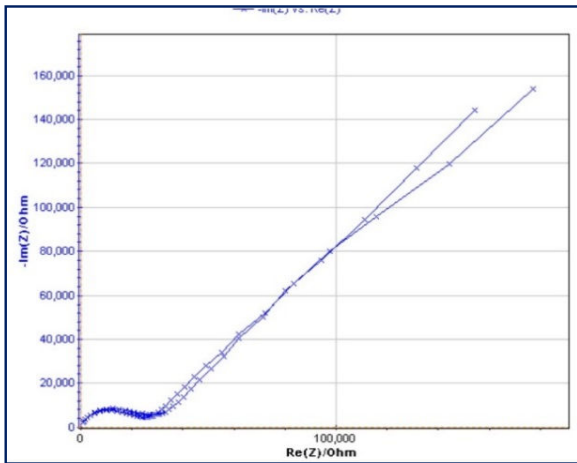


Fig. 2 Nyquist plot of the complex impedance. It shows this polymer has very low electronic conductivity and pretty high ionic conductivity

III. PERMITTIVITY, CONDUCTIVITY, AND RELAXATION

The dielectric properties provide abundant information for characterization of the electrolytes. Ionic pair relaxation, ionic conductivity, electric modulus, complex impedance and dielectric relaxation can all be evaluated and observed from the dielectric spectra.

The dielectric properties of a material can be described by a complex quantity named relative complex dielectric permittivity dependent on angular frequency ω ,

$$\hat{\epsilon}(\omega) = \epsilon'(\omega) - j\epsilon''(\omega) \quad (1)$$

where ϵ' is the real part of relative permittivity which is also called dielectric constant, ϵ'' is called dielectric loss. When applying an external electric field, the electrolyte reacts with the field proportional to the complex permittivity. While using traditional blocking two electrodes measurement or newly developed noncontact measurement, only time varying electric

field can drive the ions in the polymer electrolyte forth and back thus evaluate the ionic conductivity. In alternating field, the total current density can be presented by,

$$J_{total} = J_{conduction} + J_{displacement} = \hat{\sigma}E = -i\omega\hat{\epsilon}E \quad (2)$$

where $J_{conduction}$ is the conduction current, $J_{displacement}$ is the displacement current, and $\hat{\sigma}$ is the complex conductivity. The complex conductivity can then be transformed from the complex permittivity as

$$\hat{\sigma} = \sigma_{dc} + \sigma' + j\sigma'' = \sigma_{dc} + \omega^n \epsilon'' + j\omega\epsilon'$$

where σ_{dc} is the electronic conductivity at direct current (DC) and very small as in the ionic conducting polymer electrolyte, n is the coefficient determined by the activation energy.

The frequency dependent imaginary part of complex permittivity ϵ'' or the real part of AC complex conductivity σ' has a DC ionic conductivity plateau in a frequency range. The plateau can be extrapolated to exhibit the desired ionic conductivity of the polymer electrolytes. One way to determine this ionic relaxation is to find the loss tangent peak where indicates the ionic conductivity of the solid polymer electrolyte.

IV. MEASUREMENT METHOD

The newly developed noncontact measurement methods are based on air gap capacitor method in low frequency range and in-waveguide method in high frequency range. Comparing to the traditional contact measurement methods, these methods can acquire reliable dielectric properties. The electrodes are not contacting the electrolyte. Thus, there is no uncertainty of contact area at the interface of the electrodes and electrolytes. Also the noncontact methods prevent the electrodes metal from chemical reactions with the electrolytes.

A. Air Gap Capacitor

It is used to determine the ability of a dielectric material to store electrical energy and loss energy. The complex dielectric constant consists of a real part (ϵ'), which represents the storage capability and an imaginary part (ϵ''), which represents the loss. The ratio of the imaginary part and real part is called loss tangent or dissipation factor $\tan \delta = \epsilon'' / \epsilon'$

Dielectric constant measurements can be performed easier and faster than chemical or physical analysis techniques making them an excellent material analysis tool. The dielectric constant is defined as the ratio of the capacitance of the material to the capacitance of air, or $\epsilon' = C_x / C_0$ where C_x is capacitance with a dielectric material and C_0 is capacitance without material, or vacuum. Thus if a material is to be used for insulating purposes only, it would be better to have a lower dielectric constant, or as close to air as possible. To the contrary, if a material is to be used in electrical applications for storage of electrical charge, the higher the dielectric constant the better.

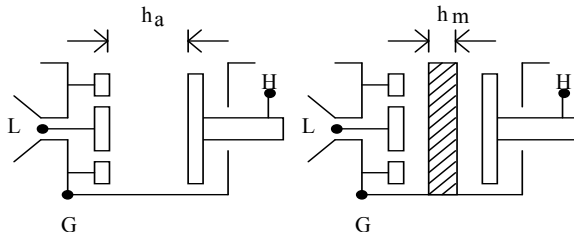


Fig. 3 Air gap capacitor method. G stands for ground. L and H indicate the two electrodes. The ground supply good shielding to the entire capacitor. Polymer electrolyte is inserted at the center of the capacitor and air gaps are between the electrolyte and electrodes to avoid contact

It is natural to hold and measure the sample by tightly clamping the electrodes. However, a layer of air between specimen and electrodes can't be completely avoided. The not full contact between polymer electrolytes and electrodes results in undesired impedance and other phenomena. A more accurate result is possible using another calculation and a specimen of known thickness. In this case the thickness of the sample is first measured at several different points and averaged to yield h_m shown in Fig. 3. The electrodes of the test cell are opened to 0.1 to 0.2 mm greater than h_m by setting the micrometer to a value of h_a . The capacitance and dissipation factor, C_a and $\tan\delta_a$, are measured for h_a , with air as the dielectric. The specimen is then inserted between the electrodes, approximately in the center, and the new values, C_{xa} and $\tan\delta_{xa}$, measured. This structure of air and specimen can be treated as series of two different capacitors by Gaussian theorem. The value for dielectric constant is then calculated from

$$\epsilon' = \left(1 - \frac{C_{xa} - C_a}{C_a} \frac{h_a}{h_m}\right)^{-1} \quad (3)$$

And dissipation factor $\tan\delta$ is calculated from

$$\tan\delta = \tan\delta_{xa} + \left(\frac{h_a}{h_m} - 1\right) \epsilon' (\tan\delta_{xa} - \tan\delta_a) \quad (4)$$

The accuracy of these results depends mainly upon the accuracy with which the thicknesses of electrolytes and distance between two electrodes can be measured.

B. In-Waveguide Method

The in-waveguide measurement is another non-contact measurement because there are no electrodes contacting the electrolyte. The polymer electrolyte is located in the waveguide as shown in Fig. 4. A propagating electromagnetic wave inside the waveguide is reflected (S_{11}) and transmitted (S_{21}) by the loaded electrolyte [8], [9]. The known electric and magnetic polarization of propagating waves in waveguides is useful in analyzing certain dielectric properties.

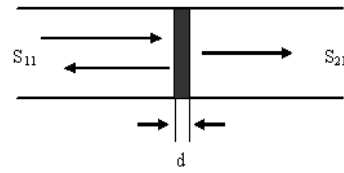


Fig. 4 Schematic diagram of electrolyte sample in waveguide

In this waveguide measurement technique, the standard thru-reflect-line calibration is used to position the reference planes. The reference planes were determined by the typical quarter wavelength difference (l) between the *thru* standard and the *line* standard. In order for the insertion phase contributions from air to be removed from the actual transmission line during the loaded material measurements, the target materials were loaded inside the waveguides adjacent to one reference plane. The modified S parameters are as follows:

$$\tilde{S}_{11} = S_{11} e^{j(0 \times \sqrt{k_0^2 - k_c^2})}, \tilde{S}_{21} = S_{21} e^{j(l-d) \times \sqrt{k_0^2 - k_c^2}} \quad (5)$$

where l is the quarter wavelength difference between *thru* and *line* (in air), d is the thickness of the sample inside the waveguide, k_0 is the wavenumber of the sample and k_c is the cutoff wavenumber. These equations take into account the effect of using samples with thickness (d) values that are smaller than the waveguide shim used in the experimental setup [2].

In the rectangular waveguide, the dominating propagating mode is the transverse electric (TE₁₀) mode. Permittivity is then calculated as follows:

$$\epsilon = -j \left(\frac{c}{f}\right)^2 \left(\frac{1-\Gamma}{1+\Gamma}\right) \left(\frac{1}{2\pi d}\right) \left(\ln\left(\frac{1}{|\Gamma|}\right) + j(2\pi n - \phi_r)\right) \cdot \left(\sqrt{\left(\frac{1}{\lambda_0}\right)^2 - \left(\frac{1}{2a}\right)^2}\right) \quad (6)$$

V. RESULTS

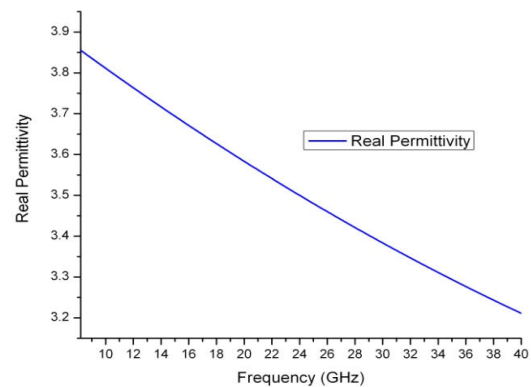


Fig. 5 Real part of relative permittivity of solid polymer electrolyte from 4 GHz to 40 GHz. The dielectric constant keeps reducing through the frequency range as the ionic relaxation weakens

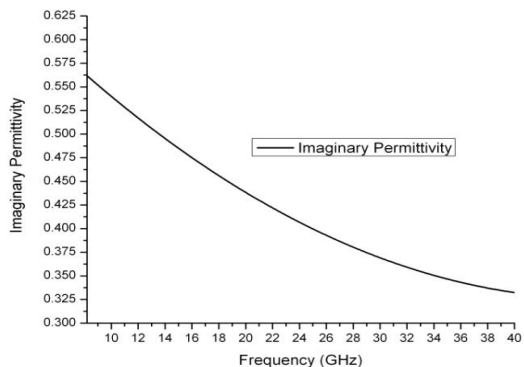


Fig. 6 Imaginary part of relative permittivity of solid polymer electrolyte from 4 GHz to 40 GHz. The field direction changes faster than the ions fully diffuse through the electrolyte. Thus the imaginary part of dielectric permittivity decreases

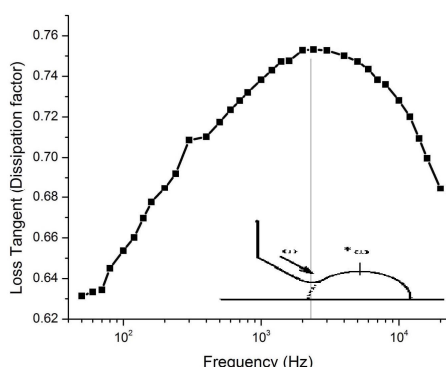


Fig. 7 A peak of loss tangent indicates the ionic relaxation. At this peak frequency, the imaginary part of permittivity determines the ionic conductivity

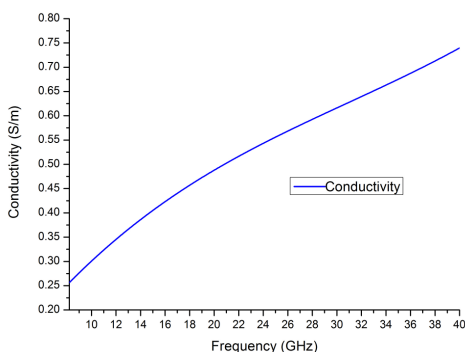


Fig. 8 Conductivity spectra of solid polymer electrolyte from 4 GHz to 40 GHz. The conductivity of the polymer electrolyte increases because of the vibration of ions

Real and imaginary permittivities from 8.2 GHz to 40 GHz are shown in Figs. 5 and 6.

Loss tangent spectra in low frequency from 50 Hz to 20 kHz are shown in Fig. 7. Real conductivity spectra measured by in-waveguide method in 4 GHz to 40 GHz are shown in Fig. 8. The Cole-Cole plot is shown in Fig. 9.

The conductivity of this polymer electrolyte is close to traditional liquid lithium electrolyte. The comparison between

contact measurement methods, liquid electrolyte will be presented later. The comprehensive result is showed in Table I.

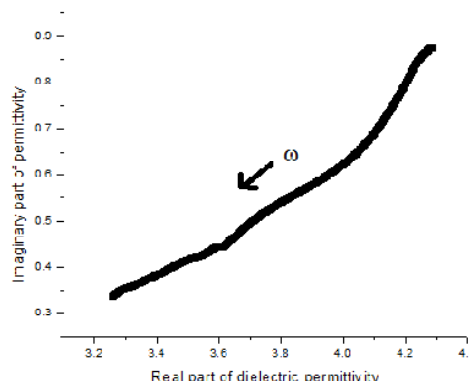


Fig. 9 Cole-Cole plot of the electrolyte in microwave frequencies. The x-axis is the real ϵ' , the y-axis ϵ'' . Essentially it is a representation of the Nyquist plot at microwave frequencies. It is the higher frequency tail of a traditional semicircle Cole- Cole plot

TABLE I
CONDUCTIVITY OF POLYMER ELECTROLYTE

Frequency	ϵ''	ϵ'	Loss	Conductivity
9.019	0.55178	3.835256	0.1438708	0.276856998
10.006	0.53999	3.811258	0.1416830	0.300591531
11.014	0.52827	3.78703	0.1394958	0.323694431
12.001	0.51712	3.76358	0.1374018	0.345256059
13.016	0.50598	3.739747	0.1352989	0.3663907
14.024	0.49525	3.716363	0.1332627	0.386392639
15.004	0.48514	3.693899	0.1313342	0.404948834
16.012	0.47505	3.671072	0.1294047	0.42317381
17.02	0.4653	3.648528	0.1275315	0.4405802
18	0.45614	3.626881	0.1257658	0.45677094
19.02	0.44693	3.604634	0.1239875	0.472911275
20.04	0.43806	3.582676	0.1222715	0.488382842
21.0175	0.42987	3.561905	0.1206868	0.502635377
22.0375	0.42166	3.540515	0.1190971	0.516963689
23.015	0.41411	3.520287	0.1176365	0.530226167
24.035	0.40657	3.499463	0.1161794	0.543631569
25.0125	0.39965	3.479778	0.1148487	0.556115153
26.0325	0.39276	3.459521	0.1135302	0.568817968
27.04	0.38629	3.439796	0.1122996	0.581096097
28.0525	0.38012	3.420258	0.1111365	0.59322192
29.065	0.37428	3.401005	0.1100485	0.605190077
30.01	0.36912	3.383292	0.1091022	0.616267686
31.0225	0.36393	3.364591	0.1081640	0.62809038
32.035	0.35906	3.346174	0.1073056	0.639920244
33.0475	0.35453	3.328043	0.1065284	0.651813454
34.06	0.35033	3.310197	0.1058341	0.663826259
35.005	0.34671	3.293797	0.1052622	0.675195622
36.0175	0.34316	3.276503	0.1047324	0.687598916
37.03	0.33993	3.259493	0.1042898	0.700286606
38.0425	0.33704	3.242768	0.1039360	0.713314864
39.055	0.33448	3.226329	0.1036725	0.726739927
40	0.33239	3.211243	0.1035092	0.739677551

VI. CONCLUSION

Complex dielectric permittivity of the novel "ceramic state" polymer electrolyte has been measured in X-band, Ku-band, K-band and Ka-band. Conductivity has been derived from the imagery part of permittivity. According to the conductivity data, this material has a quite different conduction mechanism and high conductivity close to liquid lithium electrolyte (10^{-3} S/cm at room temperature). The permittivity at this frequency range is performed between the properties of traditional polymer and ceramic materials.

The capacitance bridge with dielectric cell and vector network analyzer with waveguides exhibit the ability to implement non-contact dielectric measurement on solid lithium electrolyte polymer. The conductivity can be evaluated from the dielectric permittivity. Related ionic relaxation and ionic conductivity are then determined from the characters of the loss tangent spectra. The non-contact method avoids the contact impedance in the traditional contact method thus reduce the errors in the determination of ionic conductivity.

DFTS methods were able to successfully work out the permittivity of thin film samples for a large frequency range from 300 GHz to 800 GHz. It is thought that this method could be improved (through optical alignment, longer sampling times, or smaller sample steps) to provide data from 100 GHz to 900 GHz while also increasing resolution throughout the entire spectrum.

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