

Synthesis of Al-Al₂O₃/PVDF Core-Shell Nanodielectrics for Energy Storage Applications

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ABSTRACT

Extensive interest is being invested into the research of polymer based nanodielectrics films. Such a material provides a more practical energy storage solution primarily for embedded capacitors and can be extended for discrete capacitor devices. Achieving permittivity values K greater than 100 is difficult even with the mature ceramic-filled polymer technology. Experimentally, relative K values of 70 are considered excellent for polymer/ferroelectric composites. The concept of putting metal nanoparticles instead of ceramic comes up because metals can, in principle, be thought of as the limiting case of high permittivity particles.

We report on a cost effective and innovative method based on creating core-shell nanoparticles in polymer with aluminum (Al) nanoparticles as the high conductivity core, and a thin aluminum oxide (Al₂O₃) as capping shell for electrical insulation. The solid oxide shell around the Al core prevents agglomeration of Al nanoparticles. Results show that proper loadings of engineered oxidized aluminum (Al@Al₂O₃) in Polyvinylidene fluoride (PVDF) polymer provide high permittivity low loss nanodielectrics in par with commercially available capacitor devices along with the added structural flexibility and cost-saving to the end user.

Keywords: Nanodielectrics, PVDF, Core-shell nanoparticles, Energy storage, Polymer capacitors

1.0 INTRODUCTION

High dielectric constant (k) materials have received tremendous interest recently due to their potential applications in energy storage solutions for electronic equipment [1-3]. In particular, there is a growing demand for capacitors that can store a large amount of charge (high charge-storage capacitors), and deliver it instantaneously [4]. Such storage capacity depends on the type of materials and polarizability of the said dielectric materials. This property is enhanced by adding nanoparticles to the matrix of polymeric material that can greatly improve the thermal, mechanical and electrical properties of the nanocomposites. Further, the electrical properties of nanodielectrics can be improved if the nanoparticles are well dispersed. Since nanoparticles agglomerate easily due to high surface energy and many conventional techniques cannot break-up their agglomerates, making well dispersed discrete nanoparticles in polymer films the key issue to achieving higher performance.

1.1 METAL NANOPARTICLES

Nanodielectrics made of metal nanoparticles embedded in a polymer matrix greatly improve the properties of polymer nanocomposites used for energy storage devices. Polymers have high processing ability, mechanical flexibility, electrical breakdown strength and compatibility with several electronic technologies. However, they have a low dielectric constant (k). Embedding metal nanoparticles in a polymer matrix seems to be a very effective way to enhance the dielectric performance

of the nanocomposites [5, 6]. The dielectric constant (k) of such nanocomposites increases considerably with increasing metal nanoparticles loading into the host polymer and so does the capacitance of such composites until a specific concentration is reached, after which capacitance drops rapidly. In order to increase the energy storage capability without compromising the inter-particle spacing, we make core-shell capacitors uniformly distributed in the host polymeric films. These improved core-shell embedded devices should allow for storage of a large amount of charge per unit volume that can be released rapidly on demand.

1.1 WHY PVDF HOST MATERIAL?

Polyvinylidene fluoride or Polyvinylidene difluoride (PVDF) is being considered as dielectric in energy storage capacitors. PVDF is highly non-reactive and resistant to solvents, acids, bases, thermal heat, and has a low smoke generation during a fire event. It also has a low density (1.78) and cost less compared to the other fluoropolymers. Strong piezoelectricity was observed in PVDF, with the piezoelectric coefficient of poled (placed under a strong electric field to induce a net dipole moment) thin films as large as 6–7 pC/N: 10 times larger than that observed in any other polymer. In this paper, we will describe the use of PVDF as a polymer matrix and Al/Al₂O₃ core-shell nanoparticles for producing high dielectric (k) composite materials.

2.0 EXPERIMENTAL

The simple blending procedure in making Al@Al₂O₃/PVDF core-shell nanodielectric is shown in Figure 1.

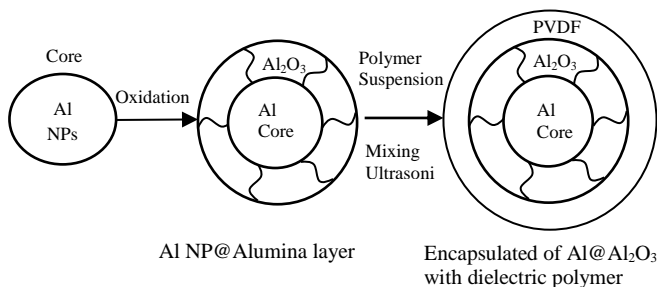


Fig.1. Fabrication steps of Al-Al₂O₃/PVDF core-shell nanodielectrics.

1. Al nanoparticles were thermally oxidized to form Al₂O₃ as capping shell for electrical insulation (figure 2). The solid oxide shell around the Al core prevents agglomeration of Al nanoparticles. Furthermore, the shell-isolated structure enhances the thermal and chemical stability of the nanoparticles, improves solubility and reactivity as well as allows conjugation of other molecules to these particles.

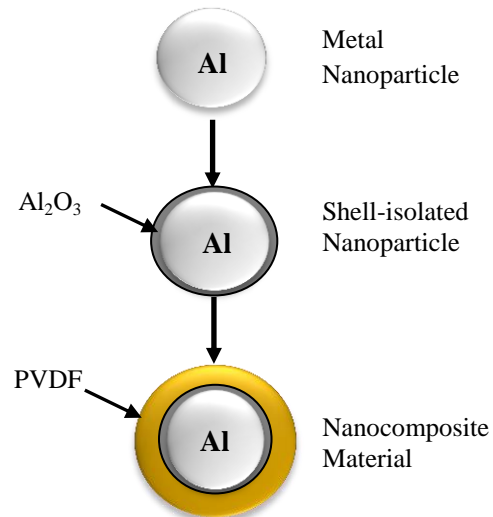


Figure 1: Representative scheme for oxide shell-isolated metal nanoparticle in PVDF polymer.

2. A solution of Al@Al₂O₃-NPs in DMF (Dimethylformamide) solvent was stirred and sonicated to completely disperse the NPs.
3. A second solution of PVDF polymer in DMF solvent was made by stirring and heating for few hours.
4. Next, these two solutions were slowly mixed and stirred for few hours on a magnetic stirrer. Finally, the mixed solution was sonicated for 2-5 minutes by a high power Mesonic sonicator to break-up the agglomerates. Prior to casting and curing the nanocomposite on silicon substrates, we first applied a thin layer of aps (3-aminopropyl triethoxysilane) solution to enhance the interfacial adhesion of PVDF.

The experimental developmental steps in making capacitor device using synthesized nanodielectrics are shown in Figure 3. The Al top electrodes were deposited through a stencil mask with 3 mm x 3mm openings which correspond to the actual size of the tested capacitors.

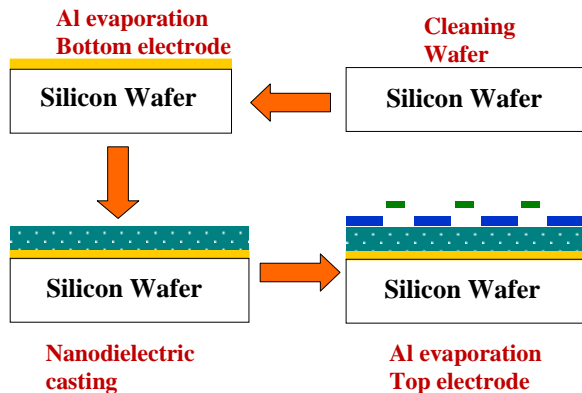


Fig.3. Fabrication steps in making planar capacitor devices.

We fabricated one capacitor using unloaded PVDF as a reference sample and two capacitors with different volume loadings of Al@Al₂O₃ fillers in PVDF host polymer. The elaborated devices were then characterized for their capacitance characteristics using an HP-4275A high frequency LCR meter. Current – Voltage measurements were obtained using Keithley 6487 picoammeter/voltage source controlled using LabView software to supply the input voltage and to read the output current. The leakage current and corresponding applied voltage till film breakdown were recorded and plotted. The thickness of the polymer was determined from the nanocomposite cross section using FEI XL-30FEG on secondary electrons microscopy measurement.

3.0 RESULTS

The high resolution SEM picture in Figure 4 shows particles size and dispersion of core-shell nanoparticles embedded in PVDF matrix. The size of nanoparticles ranges from 60 – 100 nm and the Al₂O₃ shell is about 15 nm.

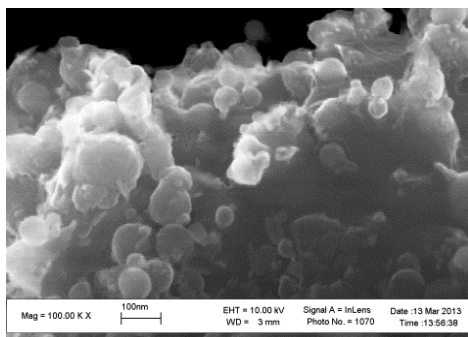


Fig.4. SEM images of Al@Al₂O₃ NPs in PVDF matrix.

Table 1 represents specifications of fabricated capacitors as well as the average value characteristics of tested capacitors at 10 KHz.

	Tested Capacitors		
	1	2	3
Capacitance (pF)	262	250	300
Thickness (nm)	3600	5500	6300
Quality factor	100	160	730
Loading (Vol. %)	0	10	20
Permittivity (K)	12	17.3	23.7

The high quality factor increases as we increase the loading of Al nanoparticles in the insulating polymer. This is most likely due to the good electrical contact forming between the top aluminum electrode and polymer nanocomposite. The permittivity of the bare PVDF is about 12 and it doubles the value for a volume loading of 20%.

Figure 5 shows the frequency behavior of typical capacitors with 3mm x 3mm Al electrodes. Each reading of the capacitance represents the average value of measurements taken on an array of 5 capacitor units. For comparison purpose, the capacitance values are normalized to the same film thickness of 6300 nm.

The electrical characterization shows reproducible and stable capacitors over frequencies up to 10 MHz.

Further studies are underway on the materials' leakage current versus breakdown voltage for nanodielectric samples of different thicknesses and different sizes of capacitor electrodes.

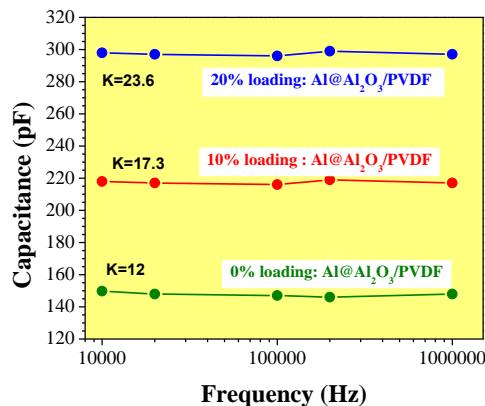


Fig.5. Dependence of capacitance on frequency for tested capacitors ranging from 150 pF to 300 pF as normalized to the same film thickness of 6300 nm.

4.0 CONCLUSIONS

We reported on a cost effective and innovative method in producing high permittivity nanodielectrics which can be easily replicable and amenable to high volume manufacturing. Results show that proper loadings of engineered oxidized aluminum (Al@Al₂O₃) in Polyvinylidene fluoride (PVDF) polymer provide high permittivity low loss nanodielectrics in par with commercially available capacitor devices along with the added structural flexibility and cost-saving to the end user.

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