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(57) Abstract: A sulfur-selenium viscoelastic alloy may have a S:Se molar ratio that ranges from about 30:70 to 60:40. A method of making a high dielectric constant viscoelastic alloy may include mixing selenium and sulfur powders together at a S:Se molar ratio that ranges from about 60:40 to 40:60; and co-melting the mixed selenium and sulfur powder. The co-melting may be performed at a temperature ranging from about 250 to 350°C.



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HIGH-K DIELECTRIC SULFUR-SELENIUM ALLOYS AND DEVICES AND METHODS THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This Application claims priority from U.S. Provisional Application No. 62/713,375, which was filed in the United States of America on August 1, 2018.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] The invention was made with government support under Grant No DE-SC0014607, awarded by the Department of Energy. The U.S. government has certain rights in the invention.

BACKGROUND OF INVENTION

[0003] Dielectric materials may be used, in forms such as insulators, capacitors, and resonators, as important passive components of electrical and electronic circuits for a wide array of applications. These applications may include, but are not limited to, energy storage, pulsed power, power conditioning, band-pass filtering, sensing, and microelectronics. The suitability of a dielectric material for use in electrical applications may be partially quantified by its dielectric constant (K), with a higher K-value providing increased capacitance. However, the current demand for “flexible” electronics technology requires components that have specific physical properties, such as viscoelasticity and strength. Thus, the commercial integration of these devices requires encapsulation with flexible and lightweight high-K materials.

[0004] Unfortunately, conventional dielectric materials, which are generally ceramics or polymers, can only provide a compromise between their dielectric and physical properties. For instance, while ceramic dielectrics such as BaTiO₃, HfO₂, SiO₂, SrTiO₃, and the like, may provide a high K-value ($20 < K < 1000$), they are also brittle materials with large losses and low breakdown voltages. In contrast, polymers such

as polyvinylidene difluoride (PVDF), polyamide (PA), rubbers, and the like, may provide a high dielectric strength and flexibility. However, they possess low-K values ($K < 15$) that limit their application in devices. Therefore, materials that can provide the best properties of both polymer and ceramic dielectrics are of great interest.

SUMMARY OF INVENTION

[0005] This summary is provided to introduce a selection of concepts that are further described below in the detailed description. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used as an aid in limiting the scope of the claimed subject matter.

[0006] In one aspect, embodiments disclosed herein relate to a device that includes a sulfur-selenium viscoelastic alloy.

[0007] In another aspect, embodiments disclosed herein relate to a method of making a high dielectric constant viscoelastic alloy that includes mixing sulfur and selenium powder together at a S:Se molar ratio between 60:40 and 40:60; and co-melting the mixed sulfur and selenium powder.

[0008] Other aspects and advantages of the claimed subject matter will be apparent from the following description and the appended claims.

BRIEF DESCRIPTION OF DRAWINGS

[0009] Figs. 1A and 1B depict calculated IR and Raman spectra, respectively, of a sulfur-selenium alloy of one or more embodiments of the present disclosure. Inset is a pictorial representation of the “transverse” arrangement of S_8 and Se_8 moieties that is postulated to provide the alloy’s unique combination of dielectric and mechanical properties.

[0010] Figs. 2A–C depict how the dielectric constant and dielectric loss, respectively, may vary with frequency for an illustrative example of a sulfur-selenium alloy of one or more embodiments. The high dielectric constant and dielectric losses in the shaded regions are due to electrode polarization.

- [0011] Figs. 3A–C present representative load-displacement data for a sulfur-selenium alloy of one or more embodiments of the present disclosure. Fig. 3A depicts load-displacement curves for compression tests performed on pure S, pure Se, and the sulfur-selenium alloy. Fig. 3B depicts the height of the sulfur-selenium alloy measured at different time intervals during recovery from application of a load. Fig. 3C depicts the variation of storage modulus, loss modulus, and damping ($\tan\delta$) of the samples with temperature. Figure 3D depicts a representative differential scanning calorimetry plot for a sulfur-selenium alloy in accordance with one or more embodiments of the present invention.
- [0012] Figs. 4A–C present images taken at different time intervals during the compression testing of, respectively, pure S, Example 1, and pure Se.
- [0013] Fig. 5 depicts the dielectric breakdown of Example 1.
- [0014] Fig. 6 presents images taken at different time intervals during the compression testing of Example 2.

DETAILED DESCRIPTION

- [0015] Embodiments disclosed herein relate generally to devices that include viscoelastic material compositions comprising sulfur and selenium. Sulfur and selenium are highly abundant and lightweight materials, but are brittle in elemental form. However, when they are co-melted in specific molar ratios, the resulting alloy may be a viscoelastic material that is ductile at room temperature and has a high dielectric constant (*e.g.*, $K \geq 20$; 1 MHz). Without being bound by a theory, it is believed that when alloyed together the S and Se atoms adopt a stable transverse arrangement that makes the alloy highly polar and giving a high dielectric constant due to the strong dipolar interactions.
- [0016] It is evident that at a frequency of 1 MHz, among common polymer dielectric materials such as polypropylene (PP), polystyrene (PS), and polyvinylidene fluoride (PVDF) ($0 < K < 10$), sulfur-selenium alloys of one or more embodiments may exhibit comparable flexibility and a superior dielectric constant. On the other hand, among the common metal oxides used in the capacitor and semiconductor industries

such as HfO_2 , Ta_2O_5 , Al_2O_3 , and SiO_2 , this material may possess a comparable dielectric constant ($0 < K < 80$) with added flexibility. Thus, the obtained S-Se alloys have polymer-like flexibility and a dielectric constant comparable to that of ceramic metal oxides.

[0017] Terms such as “approximately,” “substantially,” etc., are intended to mean that the recited characteristic, parameter, or value need not be achieved exactly, but that deviations or variations, including for example, tolerances, measurement error, measurement accuracy limitations and other factors known to those of skill in the art, may occur in amounts that do not preclude the effect the characteristic was intended to provide.

[0018] Similarly, the terms “can” and “may” and their variants are intended to be non-limiting, such that recitation that an embodiment can or may comprise certain elements or features does not exclude other embodiments of the present technology that do not contain those elements or features.

[0019] As referred to herein, all compositional percentages are specified as being by weight (wt.%) or by moles (mol%) of the total composition, unless otherwise disclosed. Disclosures of ranges are, unless specified otherwise, inclusive of endpoints and include all distinct values and further divided ranges within the entire range.

[0020] SULFUR–SELENIUM ALLOY COMPOSITIONS

[0021] Two common nonpolar, brittle constituents, sulfur (S) and selenium (Se) may be combined through a facile co-melting process to provide a sulfur-selenium alloy. In one or more embodiments, the sulfur-selenium alloy according to the present disclosure may comprise S in an amount ranging from about 30 to 62 mol%. In some embodiments, the sulfur-selenium alloy may comprise S in an amount that ranges from a lower limit selected from 30, 35, 37, 38, and 39 mol%, to an upper limit selected from 62, 60, 58, 55, 53, 50, 45 and 40 mol%, where any lower limit may be paired with any mathematically-compatible upper limit.

[0022] In one or more embodiments, the sulfur-selenium alloy according to the present disclosure may comprise Se in an amount ranging from about 38 to 70

mol%. In some embodiments, the sulfur-selenium alloy may comprise Se in an amount that ranges from a lower limit selected from 38, 39, 40, 45, 50, and 60 mol%, to an upper limit selected from 70, 65, 64, 63, 60, 55, 50, 45 and 40 mol%, where any lower limit may be paired with any mathematically-compatible upper limit.

[0023] In one or more embodiments, the sulfur-selenium alloy according to the present disclosure may have a molar ratio of S:Se from about 30:70 to 60:40. In some embodiments, the sulfur-selenium alloy may have a molar ratio of S:Se that ranges from a lower limit selected from 30:70, 35:65, 38:62, 40:60, 45:55, and 49:51, to an upper limit selected from 45:55, 50:50, 51:49, 55:45, and 60:40, where any lower limit may be paired with any mathematically-compatible upper limit. In particular embodiments, the sulfur-selenium alloy may have a molar ratio of S:Se of about 50:50.

[0024] In some embodiments, the elemental composition of sulfur-selenium alloys may be determined by X-ray photoelectron spectroscopy (XPS).

[0025] The sulfur-selenium alloy in accordance with one or more embodiments of the present disclosure may comprise one or more additives. One of ordinary skill in the art will appreciate, with the benefit of this disclosure, that the choice of additive may be dependent upon the intended use of the composition and/or devices produced therefrom. It will also be appreciated that such additives are not limited to those described below.

[0026] Such additives may be selected from lithium, silicon, and carbonaceous additives (e.g., carbon nanotubes, activated carbon, graphite, graphene, reduced graphene oxide, and the like). In particular embodiments, the additives may be selected from reduced graphene oxide, activated carbon, and carbon nanotubes. In one or more embodiments, the addition of carbon nanotubes, activated carbon, and/or graphene may increase the conductivity of the sulfur-selenium alloy, which may be useful in making a flexible cathode material for battery applications (e.g., Li-S batteries).

[0027] The sulfur-selenium alloy in accordance with one or more embodiments of the present disclosure may comprise a total amount of additives of 25 wt.% or less, 20

wt.%, or less, 15 wt.% or less, 10 wt.% or less, 5 wt.% or less, or 2.5 wt.% or less. In one or more embodiments, the minimum amount of additional additive may be at least 0.1 wt.%, at least 0.5 wt.%, at least 1 wt.%, or at least 1.5 wt.%.

[0028] **PROPERTIES AND CHARACTERIZATION**

[0029] The properties of a sulfur-selenium alloy in accordance with the present disclosure will generally be suitable for the alloy's intended use. One of ordinary skill in the art will, with the benefit of this present disclosure, appreciate that altering the relative amounts and/or identities of the components of a composition will influence the properties of the composition or an article or device formed therefrom.

[0030] Characterization of S–Se Alloys

[0031] In one or more embodiments, Raman spectra of a sulfur-selenium alloy in accordance with the present disclosure may exhibit two peaks that correspond to S–Se bond vibrations. In some embodiments, one of the two vibrations has an energy of the range of 250 to 260 cm^{-1} . In some embodiments, one of the two vibrations has an energy of the range of 345 to 355 cm^{-1} . Generally, the S–Se vibrations can be distinguished from Se–Se phonon vibrations, though, in some embodiments, the Se–Se vibrations in the sulfur-selenium alloy may be shifted to a higher energy as compared to the same vibrations in pure Se. In one or more embodiments, the shift in Se–Se vibration energy may be of the range of about 3 to 8 cm^{-1} . In some embodiments, the shift is of about 5 cm^{-1} .

[0032] In one or more embodiments, a sulfur-selenium alloy in accordance with the present disclosure may possess a monoclinic structure, as determined by X-ray diffraction (XRD). In some embodiments, a sulfur-selenium alloy may be semi-crystalline. In such embodiments, residual Se, which typically has a hexagonal structure, may be observed as a background signal in the XRD data.

[0033] In some embodiments, sulfur-selenium alloys may principally contain sulfur and selenium as their octasulfur (S_8) and octaselenium (Se_8) allotropes, respectively. One of ordinary skill in the art will appreciate, with the benefit of this disclosure, that the principal allotropes present in the alloy will depend upon the temperatures applied during synthesis *vide infra*. In one or more embodiments, sulfur-selenium

alloys may comprise a recurring sulfur-selenium unit. The recurring unit, in some embodiments, may comprise a S₈ and a Se₈ molecule orientated transversely (perpendicularly) to each other. *See* Figs. 1A–1B. The sulfur-selenium unit may have a dipole moment, with the S₈ being negatively charged and the Se₈ being positively charged. One of ordinary skill in the art will appreciate, with the benefit of this disclosure, that the molecular arrangement of the sulfur and the selenium will heavily influence the dielectric properties of the alloy.

[0034] The thermal stability of a sulfur-selenium alloy in accordance with the present disclosure may be determined by thermogravimetric analysis (TGA). In some embodiments, TGA may be performed under an inert atmosphere and with a temperature ramp of 10°C/min from 30° to 650°C. In one or more embodiments, a sulfur-selenium alloy in accordance with the present disclosure may possess a thermal stability that lies in between S and Se. As used herein, “thermal stability” refers to the compositional stability of an alloy. In some embodiments, a sulfur-selenium alloy may thermally degrade at a temperature ranging from 560 to 580 K. In particular embodiments, the sulfur-selenium alloy may thermally degrade at a temperature ranging from 570 to 575 K. In some embodiments, the sulfur-selenium alloy may be thermally stable up to a temperature of at least 500 K, at least 520 K, at least 540 K, at least 550 K, at least 560 K, at least 570 K, or at least 580 K.

[0035] Dielectric Properties

[0036] As discussed above, and without being bound to any theory, the molecular arrangement of the sulfur and the selenium may, in some embodiments, involve the transverse orientation of S₈ and Se₈ moieties. Such an orientation may provide a charge delocalization between the S and Se atoms, resulting in a significant dipole moment.

[0037] In one or more embodiments, the dielectric constant (K) of the sulfur-selenium alloy may, at a frequency of 1 MHz, be at least 25, at least 35, at least 45, at least 55, at least 65, at least 70, or at least 72. In some embodiments, the dielectric constant of the sulfur-selenium alloys may remain substantially constant in the 1 kHz to 1 MHz frequency range. *See* Fig. 2A. The dielectric constant of the sulfur-selenium alloy of one or more embodiments may decrease as the frequency is increased

beyond 1 MHz. In one or more embodiments, the dielectric constant of the sulfur-selenium alloy may be at least 3, at least 4, at least 4.5, or at least 5 at a frequency of 100 GHz. *See Fig. 2B*

[0038] In some embodiments, the dielectric constant of sulfur-selenium alloys may be similar for samples with different thicknesses in the 1 kHz to 1 MHz frequency range. In one or more embodiments, samples that differ in thickness by a factor of 5 or more, 6 or more, 7 or more, or 8 or more, may have dielectric constants that differ by 15% or less, 12% or less, 10% or less, or 9% or less. In one or more embodiments, the dielectric constant of a sulfur-selenium alloy may be estimated by calculating the capacitance of the material obtained by a complex impedance measurement.

[0039] In one or more embodiments, the dielectric loss of the sulfur-selenium alloys in accordance with the present disclosure may, at a frequency of 1 MHz, be at most 0.1, at most 0.01, at most 0.005, or at most 0.001. *See Fig. 2C*. In some embodiments, the dielectric loss of the sulfur-selenium alloys may remain substantially constant in the 1 kHz to 1 MHz frequency range. The dielectric loss of the sulfur-selenium alloy of one or more embodiments may increase as the frequency is increased. In one or more embodiments, the dielectric loss of the sulfur-selenium alloy may be at least 0.32, at least 0.34, or at least 0.36, at a frequency of 100 GHz. In one or more embodiments, the dielectric loss of the sulfur-selenium alloy may be at most 0.38, at most 0.40, or at most 0.42, at a frequency of 100 GHz. The dielectric loss may be calculated by the phase difference in the impedance at various frequencies.

[0040] In one or more embodiments, the dielectric strength of the sulfur-selenium alloys in accordance with the present disclosure may be at least 35 kV/mm, at least 38 kV/mm, or at least 40 kV/mm. In some embodiments, the dielectric strength of the sulfur-selenium alloys in accordance with the present disclosure may range from about 35 to 45 kV/mm. In particular embodiments, the dielectric strength of the sulfur-selenium alloys may range from about 38 to 42 kV/mm.

[0041] In one or more embodiments, at a higher bias voltage (1 V), the capacitance of a sulfur-selenium alloy may be reduced. This may occur because the alloy of one or

more embodiments changes shape upon application of an electrical potential, a common phenomenon observed for dielectric elastomers.

[0042] Physical Properties

[0043] In one or more embodiments, sulfur-selenium alloys in accordance with the present disclosure may exhibit a far greater resistance to compression, and be less brittle, than pure S and pure Se. It is thought, without being bound by any theory, that the local interaction of Se₈ and S₈ rings in the alloy results in not only the high polarization between S₈ and Se₈ discussed above, but also a high resistance to mechanical compression resulting from repulsion between the dipole moments of the Se₈ and Se₈ moieties.

[0044] In some embodiments, sulfur-selenium alloys may, upon the application of a load, undergo a high-strain deformation to provide a thin sheet. The sheet may subsequently recover its original shape upon removal of the load. For example, *see* Fig. 4B. In one or more embodiments, the compressive properties of sulfur-selenium alloys may be measured in accordance with ASTM D1621. In some embodiments, sulfur-selenium alloys in accordance with the present disclosure may be able to withstand loads of up to 10 kN, up to 15 kN, up to 20 kN, or up to 25 kN without fracturing. *See* Fig. 3A. In some embodiments, sulfur-selenium alloys in accordance with the present disclosure may be able to withstand strains of up to 0.2 GPa, up to 0.3 GPa, or up to 0.4 GPa.

[0045] In some embodiments, sulfur-selenium alloys may, after the application of a load, exhibit a mechanical recovery of strain ranging from 30 to 50%, or from 35 to 45%, immediately after the release of the load. In one or more embodiments, sulfur-selenium alloys may exhibit a mechanical recovery of strain of at least 90%, at least 93%, at least 95%, or at least 96% after the load has been removed for 10 minutes. The mechanical recovery may be quantified by monitoring the height of the sample before, during, and after, the application of a load. In some embodiments, the mechanical recovery may be measured in accordance with ASTM D1621. For example, *see* Fig. 3B.

[0046] In some embodiments, sulfur-selenium alloys may exhibit viscoelastic behavior, as determined by a dynamic mechanical analysis (DMA). In one or more

embodiments, the storage, loss, and dynamic modulus of sulfur-selenium alloys may be determined by temperature-dependent DMA cyclic tensile tests. In some embodiments, said tests may be performed over a temperature range of -20 to 60°C .

[0047] At 25°C , the sulfur-selenium alloy of one or more embodiments may possess a storage modulus that ranges from a lower limit selected from 110, 120, 130, 140, 145, or 150 MPa to an upper limit selected from 150, 155, 160, 170, or 180 MPa, where any lower limit may be paired with any mathematically-compatible upper limit.

[0048] At 25°C , the sulfur-selenium alloy of one or more embodiments may possess a loss modulus that ranges from a lower limit selected from 60, 70, 75 or 80 MPa to an upper limit selected from 80, 85, 90, or 100 MPa, where any lower limit may be paired with any mathematically-compatible upper limit.

[0049] At 25°C , the sulfur-selenium alloy of one or more embodiments may possess a dynamic modulus that ranges from a lower limit selected from 150, 160, 165, or 170 MPa to an upper limit selected from 170, 175, 180, or 190 MPa, where any lower limit may be paired with any mathematically-compatible upper limit.

[0050] In one or more embodiments, sulfur-selenium alloys may possess a Young's modulus, as determined by DMA, that ranges from a lower limit selected from 2.0, 2.5, 2.8, or 3.0 GPa to an upper limit selected from 3.0, 3.2, 3.5, or 4.0 GPa, where any lower limit may be paired with any mathematically-compatible upper limit.

[0051] In one or more embodiments, sulfur-selenium alloys may possess a glass transition temperature (T_g) that ranges from a lower limit selected from 5, 7, 8, 9, or 10°C to an upper limit selected from 10, 11, 12, 13, or 15°C , where any lower limit may be paired with any mathematically-compatible upper limit. The T_g may be measured by differential scanning calorimetry. For a representative example, please see Fig. 3D. Thus, in some embodiments, sulfur-selenium alloys may behave elastically at room temperature (as room temperature may be above T_g).

[0052] In one or more embodiments, the sulfur-selenium alloy may be operationally viable at temperatures that range from about 16 to 180°C . At temperatures below these ranges, the alloy may become brittle. At temperatures above these ranges, the

alloy may become more fluid-like. One of ordinary skill in the art will appreciate, with the benefit of this disclosure, that the operational window of the sulfur-selenium alloys may be tuned for a specific application by the inclusion of the (non-limiting) additives discussed above.

[0053] METHODS

[0054] In one or more embodiments, sulfur-selenium alloys in accordance with the present disclosure may be prepared by a facile and scalable co-melting process. S and Se are miscible in all ratios and form chalcogenide alloys. In one or more embodiments, the alloys may be prepared by any known method of mixing sulfur, selenium, and the other components (if any). The mixing may be performed homogenously, in some embodiments, with a pestle and mortar. In particular embodiments, the mixing step is performed homogeneously in the solid state, yielding a ground powder mixture of S and Se. In one or more embodiments, additives may be mixed simultaneously with the sulfur and selenium. In some embodiments, the sulfur and selenium may be mixed first, and any additional components may be mixed in subsequently.

[0055] Following the mixing step of one or more embodiments, the mixture may be co-melted. The co-melting may comprise heating the mixture at a temperature that ranges from about 250°C to 350°C. In some embodiments, the temperature may range from a lower limit selected from 250, 260, 270, 280, 290, 295, and 300°C, to an upper limit selected from 300, 305, 310, 320, 330, 340, and 350°C, where any lower limit may be paired with any mathematically-compatible upper limit. The co-melting temperature may influence the structure and the properties of the resulting sulfur-selenium alloy. In one or more embodiments, the co-melting temperature is a temperature at which octasulfur (S₈) and octaselenium (Se₈) are the most abundant and stable allotropes of the respective elements. It may be envisioned that variation of the co-melting temperature may influence the stability and relative abundance of the various allotropes of S and Se, resulting in alloys that may possess different molecular structures.

[0056] In one or more embodiments, the heating may be performed for a time that ranges from about 25 to 35 minutes. In some embodiments, the heating may be

performed for a time that ranges from a lower limit selected from 15, 20, 25, and 30 minutes, to an upper limit selected from 30, 35, 40, and 45 minutes, where any lower limit may be paired with any mathematically-compatible upper limit.

[0057] In one or more embodiments, the sulfur-selenium alloy according to the present disclosure may be prepared by mixing relative amounts of S and Se in a molar ratio S:Se that ranges from about 45:55 to 55:45. In some embodiments, the sulfur-selenium alloy may be prepared by mixing relative amounts of S and Se in a molar ratio S:Se that ranges from a lower limit selected from 40:60, 45:55, 46:54, 47:53, 48:52, and 49:51, to an upper limit selected from 51:49, 52:48, 53:47, 54:46, 55:45, and 60:40, where any lower limit may be paired with any upper limit. In particular embodiments, the sulfur-selenium alloy may be prepared by mixing equimolar amounts of S and Se, *i.e.* the molar ratio S:Se of about 50:50.

[0058] DEVICES

[0059] Sulfur-selenium alloys in accordance with one or more embodiments of the present disclosure may be used for dielectric applications in semiconductor industries. In terms of device applications, a sulfur-selenium alloy of one or more embodiments may be used as a component in a solid-state electrolyte system for rechargeable Li-ion batteries, as an electrical insulator, as an encapsulant of electrical circuits in, for example, flexible energy devices, as a capacitor, or as actuators, for applications such as artificial muscles, because the alloys may change shape upon the application of a voltage.

[0060] In one or more embodiments, the sulfur-selenium alloy may be used as a cathode in a battery. In some embodiments, the battery may be a Li-ion battery. The charge-discharge voltage profiles of the cathodes of one or more embodiments may exhibit a charge cycling behavior that provides an excellent coulombic efficiency of ~99% over 50 cycles or more, 75 cycles or more, 100 cycles or more, or 200 cycles or more, at a current rate of 0.1 C.

[0061]

[0062] EXAMPLES

[0063] The following examples are merely illustrative and should not be interpreted as limiting the scope of the present disclosure.

[0064] Sample preparation

[0065] Example 1: commercial S (99.99%; Sigma-Aldrich) and Se (99.99%; Sigma-Aldrich) were taken in an equimolar ratio (*i.e.* a S:Se molar ratio of 50:50) and mixed together in a mortar and pestle. The obtained powder was placed in an alumina boat and co-melted in the furnace at a temperature of 573 K (300°C) for 30 min in an Ar atmosphere. After the sample was cooled, it was taken out of the alumina mold.

[0066] Example 2: was prepared in the same way as Example 1 except equal masses (*i.e.* a S:Se molar ratio of 29:71) of S and Se were used.

~~[0067]~~— The as-synthesized products were cut into cubes (8.67 mm × 8.67 mm × 4.25 mm) with a sharp blade to provide samples for measuring mechanical properties. The samples were also polished slightly to ensure a flat surface for mechanical testing. The sample for pressure testing was formed by casting the melt of S and Se at 513.15 K in a 1-mm-diameter stainless steel mold and was taken out of the mold by a punch. Samples (4.00mm× 4.900mm× 0.374mm) were used for measuring dielectric properties using impedance spectroscopy. As-cast samples were recasted as thin films on the Al foil, and samples of the given dimensions were cut with a blade out of the cast. Au (10 nm) was sputtered on both sides of the samples. The Au-coated samples were placed in stainless steel load cell, and impedance was measured at 0-V bias in a frequency range of 1Hz to 1 MHz. For higher-frequency measurements (100 GHz) and dielectric strength measurements, samples (2 mm × 0.6mm) were prepared by melting them in the corresponding Al mold.

[0068] Measuring dielectric properties

[0069] The existence of a dipole moment in Example 1 was experimentally verified by measuring the complex impedance on an Autolab 302 electrochemical workstation using the module FRA32M. The dielectric constant of the S-Se alloy was estimated by calculating the capacitance of the material obtained in the

impedance measurement. For this purpose, 10 nm of Au was coated on the top and bottom surfaces and the impedance measurement was carried out.

[0070] The dielectric strength of Example 1 was determined by inserting the sample between two electrodes that had an approximate radius of 4 mm and an electrode gap spacing of 1 mm, with a high-voltage power supply (HVPS) connected to the electrodes. The measured dielectric strength of the alloy (40 kV/mm) is comparable to that of the common polymer dielectric materials such as PP, PS, and PVDF ($0 < \text{dielectric strength} < 60 \text{ kV/mm}$). See Fig. 5 for the dielectric breakdown of Example 1.

[0071] Results and Discussion

[0072] Table 1: Comparison of Example 1 and Example 2

	Composition (%)		Raman (cm⁻¹)	Mechanical Properties
	S	Se		
Ex. 1	38.96	61.04	239 255 351	Viscoelastic
Ex. 2	62.96	37.04	252 374 450	Ductile

[0073] Compression tests conducted on pure S and Se show that they fracture easily upon application of load and display brittle behavior. See Figs. 4A and 4C. On the other hand, when the load is applied to Example 1, instead of fracturing, it undergoes high-strain deformation to a thin sheet and recovers its original shape upon removal of load. See Fig. 4B. However, such behavior is not exhibited by Example 2 which instead demonstrates ductile behavior. See Fig. 5.

[0074] Table 2: Physical and Dielectric Properties of Example 1

T_g	$9.83 \pm 1.14 \text{ }^\circ\text{C}$
Storage Modulus (@ 25°C)	150 MPa
Loss Modulus (@ 25°C)	80 MPa
Dynamic Modulus (@ 25°C)	170 MPa
Young's Modulus	3 GPa
Mechanical Recovery	96%
Dielectric Constant (@ 1 MHz)	74
Dielectric Constant (@ 100 GHz)	4.5

Dielectric Loss (@ 1 MHz)	0.001
Dielectric Loss (@ 100 GHz)	0.8
Dielectric Strength	40 kV/mm

[0075] Table 3: Dielectric Constant of Example 1 at Different Thicknesses

Thickness (mm)	Dielectric Constant at 1 MHz
0.05	67
0.08	68
0.3	75
0.4	73

[0076] Example 1 exhibits ceramic-like dielectric properties and polymer-like viscoelastic behavior and mechanical flexibility. The dielectric constant ($K = 74$ at 1 MHz) and the dielectric strength (40 kV/mm) are comparable to some of the conventional metal oxides ($0 < K < 80$) and 10 times higher than polymers ($1 < K < 10$). It is interesting to note that pure S and Se are nonpolar with dielectric constants of 3 and 6, respectively. Thus, there is a 13 times increase in the dielectric constant as compared to the individual components S and Se. Furthermore, Example 1 exhibits unique mechanical behavior including viscoelasticity with excellent mechanical recovery (96%), a high Young's modulus among polymers (3 GPa), and a T_g ($9.83 \pm 1.14^\circ\text{C}$), which is below room temperature.

[0077] Chalcogen alloys in accordance with one or more embodiments of the present disclosure could fill the gap for soft high-K dielectric materials in several flexible device applications. Significantly, sulfur-selenium alloys may have a dielectric constant that is higher than conventional metal oxide ceramics (*e.g.* HfO_2) while simultaneously providing a flexibility like rubbery polymers such as PVDF.

[0078] Although only a few example embodiments have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the example embodiments without materially departing from this invention. Accordingly, all such modifications are intended to be included within the scope of this disclosure as defined in the following claims.

CLAIMS

What is claimed is:

1. A composition, comprising:
a sulfur-selenium viscoelastic alloy.
2. The composition of claim 1, wherein the sulfur-selenium viscoelastic alloy has a S:Se molar ratio that ranges from about 30:70 to 60:40.
3. The composition of claim 1 or claim 2, wherein the sulfur-selenium viscoelastic alloy further comprises one or more additives selected from the group consisting of lithium, silicon, and carbonaceous additives.
4. The composition of claim 3, wherein the sulfur-selenium viscoelastic alloy comprises the one or more additives in an amount of at most 25 wt.%.
5. The composition of claim 3 or 4, wherein the sulfur-selenium viscoelastic alloy comprises the one or more additives in an amount of at least 0.1 wt.%.
6. The composition of any of the above claims, wherein the sulfur-selenium viscoelastic alloy has a dielectric constant greater than or equal to 45 when measured at 1 MHz.
7. The composition of claim 6, wherein the sulfur-selenium viscoelastic alloy has a dielectric constant greater than or equal to 65 when measured at 1 MHz.
8. The composition of any of the above claims, wherein the sulfur-selenium viscoelastic alloy has a dielectric constant of at least 3 when measured at 100 GHz.
9. The composition of claim 8 wherein the sulfur-selenium viscoelastic alloy has a dielectric constant of at least 4 when measured at 100 GHz.
10. The composition of any of the above claims, wherein the sulfur-selenium viscoelastic alloy has a dielectric loss of 0.001 or less when measured at 1 MHz.

11. The composition of any of the above claims, wherein the sulfur-selenium viscoelastic alloy has a dielectric loss that ranges from about 0.36 to 0.42 when measured at 100 GHz.
12. The composition of any of the above claims, wherein the sulfur-selenium viscoelastic alloy has a dielectric strength of at least 35 kV/mm.
13. The composition of any of the above claims, wherein the sulfur-selenium viscoelastic alloy has a glass transition temperature (T_g) that ranges from about 5 to 15°C.
14. The composition of any of the above claims, wherein the sulfur-selenium viscoelastic alloy is thermally stable up to a temperature of at least 560 K.
15. The composition of any of the above claims, wherein the composition consists essentially of the sulfur-selenium viscoelastic alloy.
16. A device comprising the composition of any of the above claims.
17. The device of claim 15, wherein the device is selected from the group consisting of a Li-ion battery, a flexible energy device, a capacitor, and an actuator.
18. The device of claim 15, wherein the device is a capacitor and at least a portion of the capacitance of the capacitor is provided by the sulfur-selenium viscoelastic alloy.
19. The device of claim 15, wherein the device comprises an electrical circuit and at least a portion of the circuit is encapsulated with the sulfur-selenium viscoelastic alloy.
20. The device of claim 15, wherein the device is an actuator that comprises the sulfur-selenium viscoelastic alloy, and wherein the sulfur-selenium viscoelastic alloy changes shape upon the application of a potential difference.
21. The device of claim 15, wherein the device comprises one or more electrical components that are electrically insulated by the sulfur-selenium viscoelastic alloy.
22. The device of claim 15, wherein the device is a Li-ion battery, and wherein the battery comprises an electrode that comprises the sulfur-selenium viscoelastic alloy.

23. A method of making a high dielectric constant viscoelastic alloy, comprising:
mixing selenium and sulfur together in a S:Se molar ratio that ranges from about 60:40 to 40:60 to provide a mixed selenium and sulfur powder; and
co-melting the mixed selenium and sulfur powder.
24. The method of claim 23, wherein the mixed selenium and sulfur powder are co-melted at a temperature that ranges from about 250 °C to 350 °C.
25. The method of claim 23 or 24, wherein the co-melting is performed for a time that ranges from about 20 to 40 minutes.

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FIG. 1A

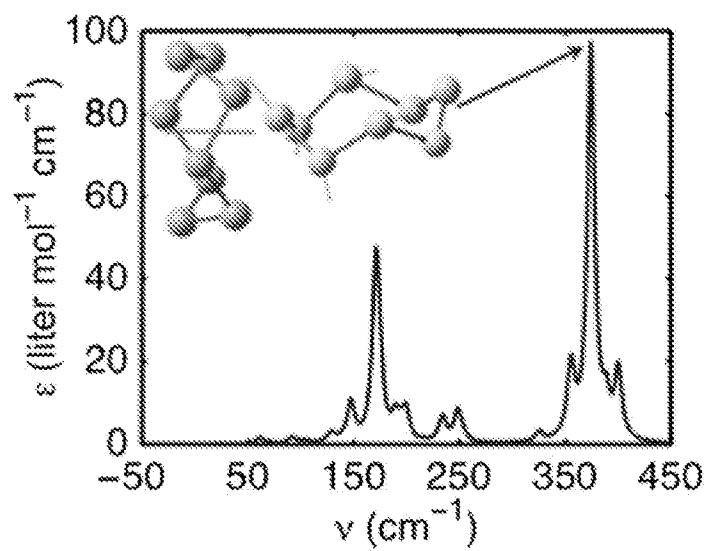
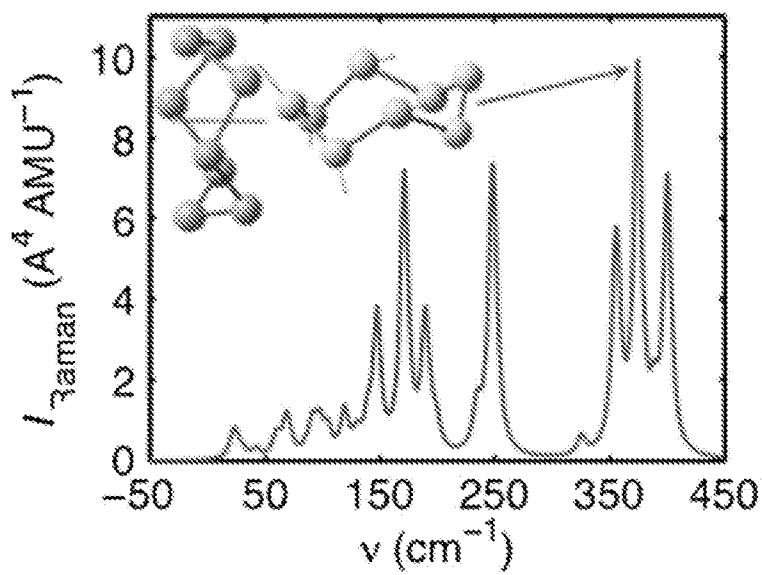


FIG. 1B



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FIG. 2A

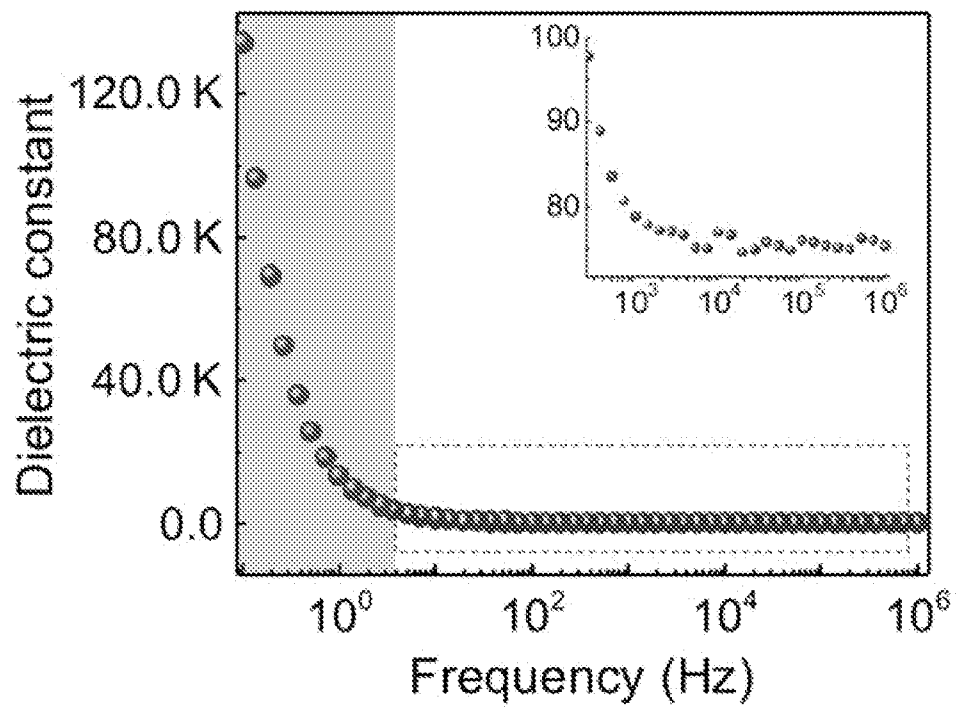
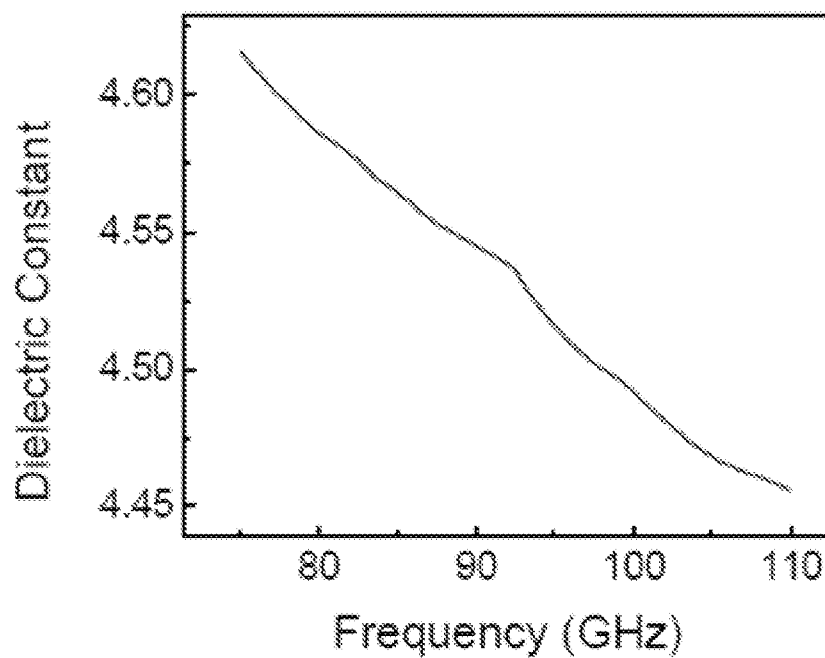
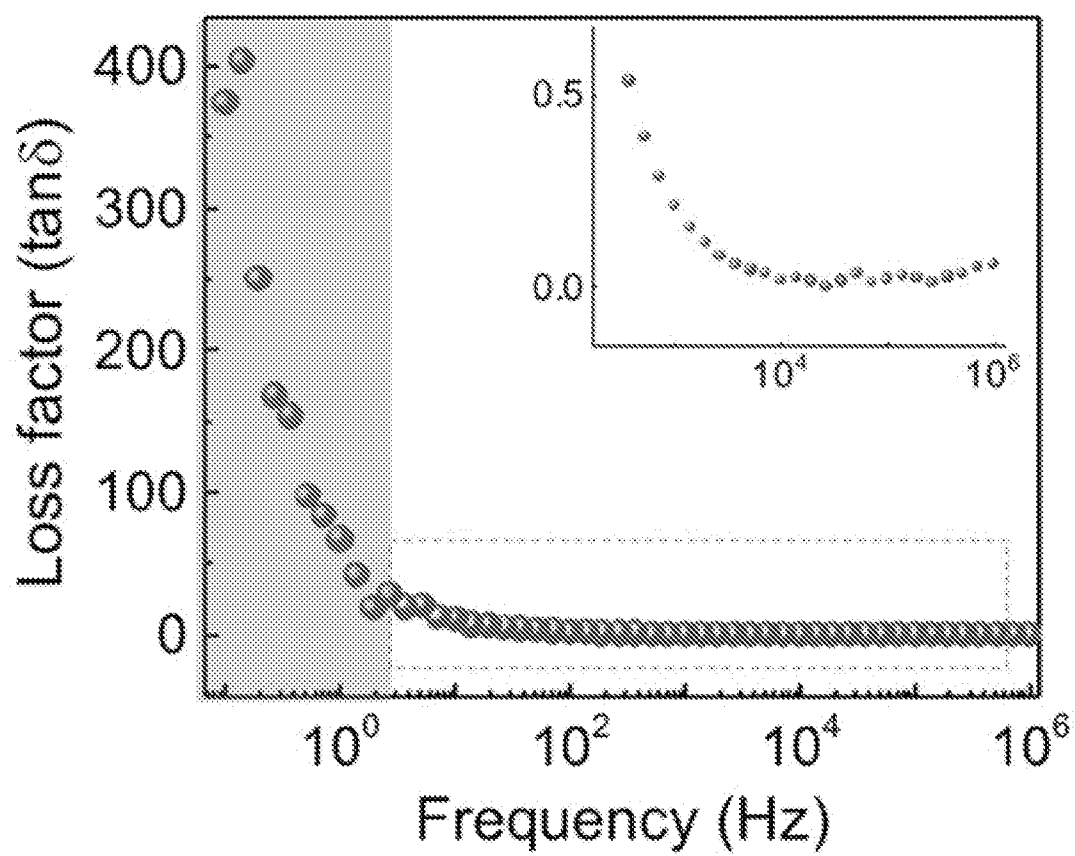


FIG. 2B



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FIG. 2C



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FIG. 3A

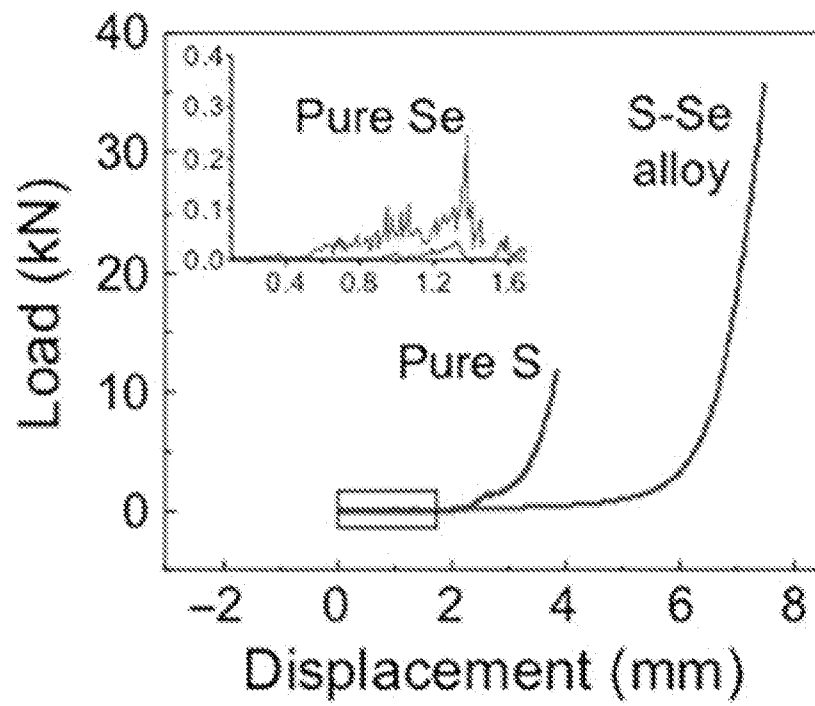
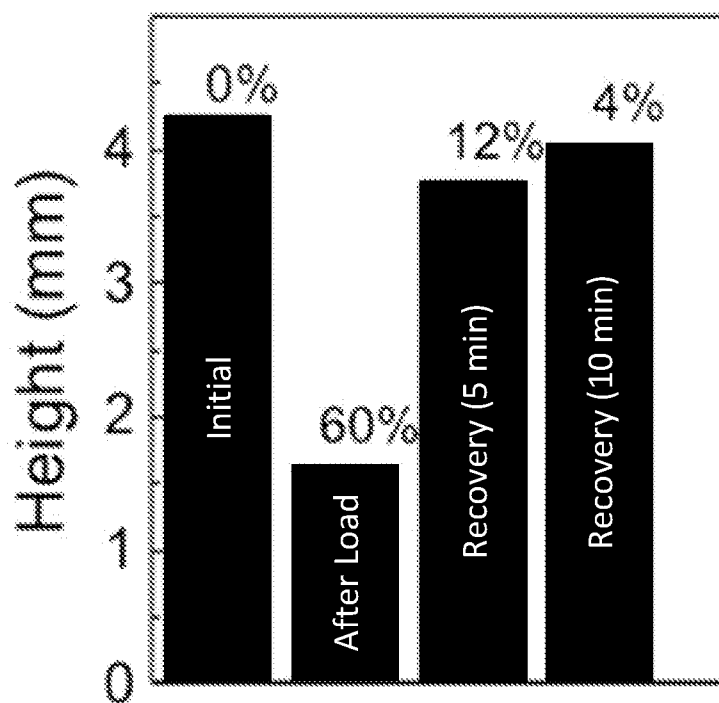


FIG. 3B



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FIG. 3C

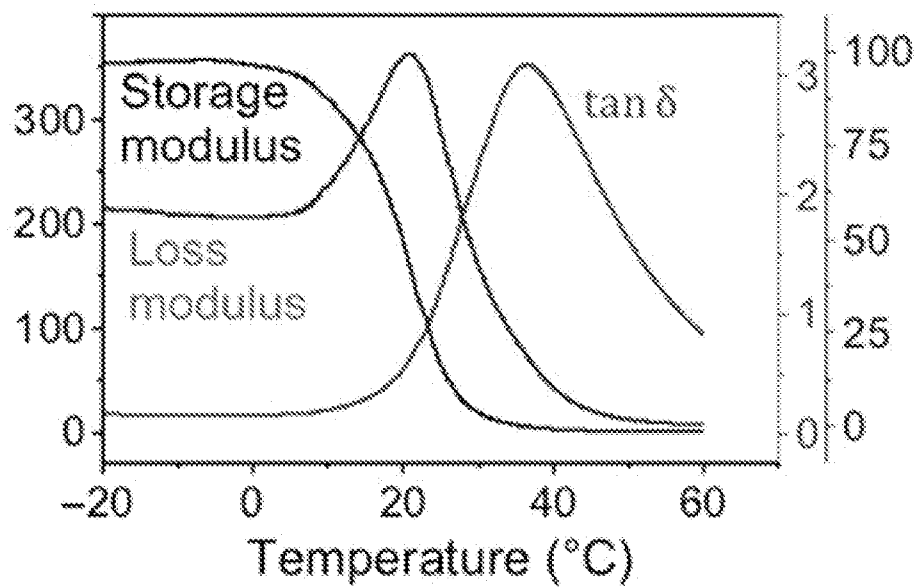
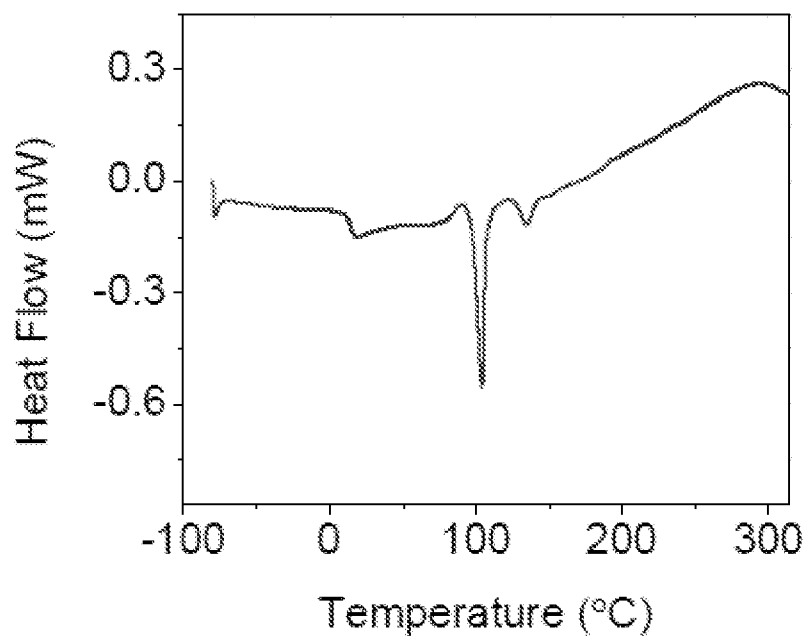


FIG. 3D



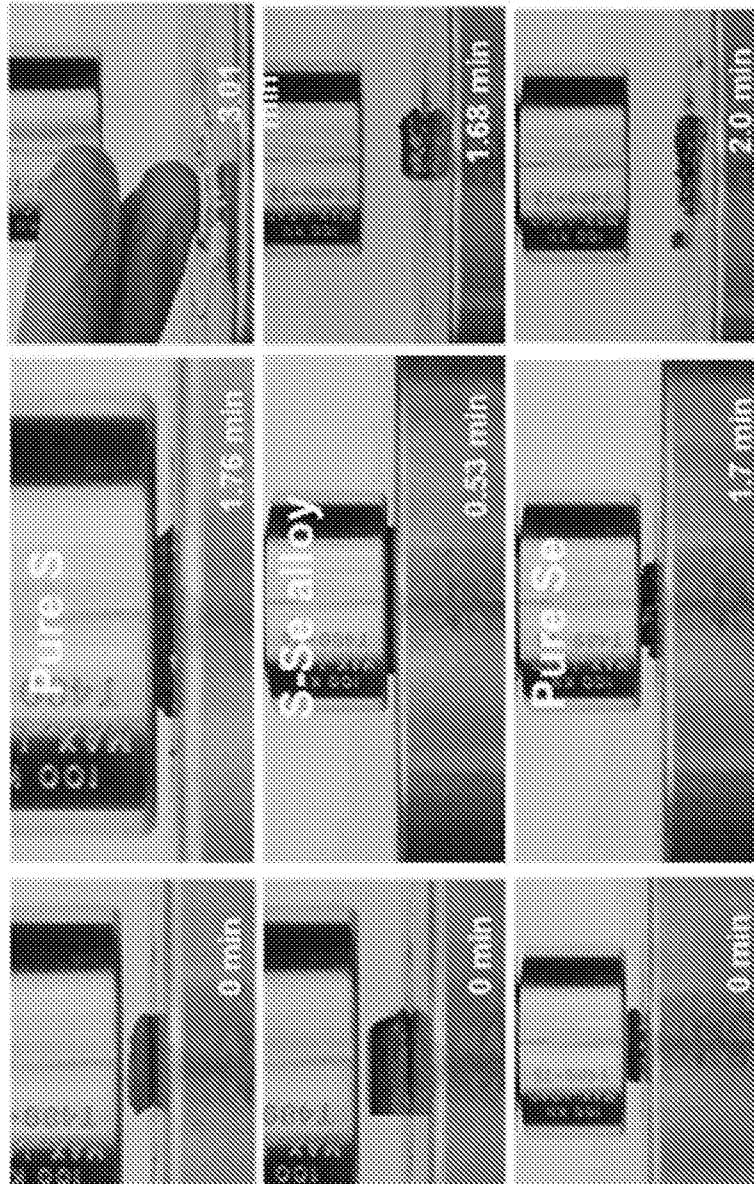


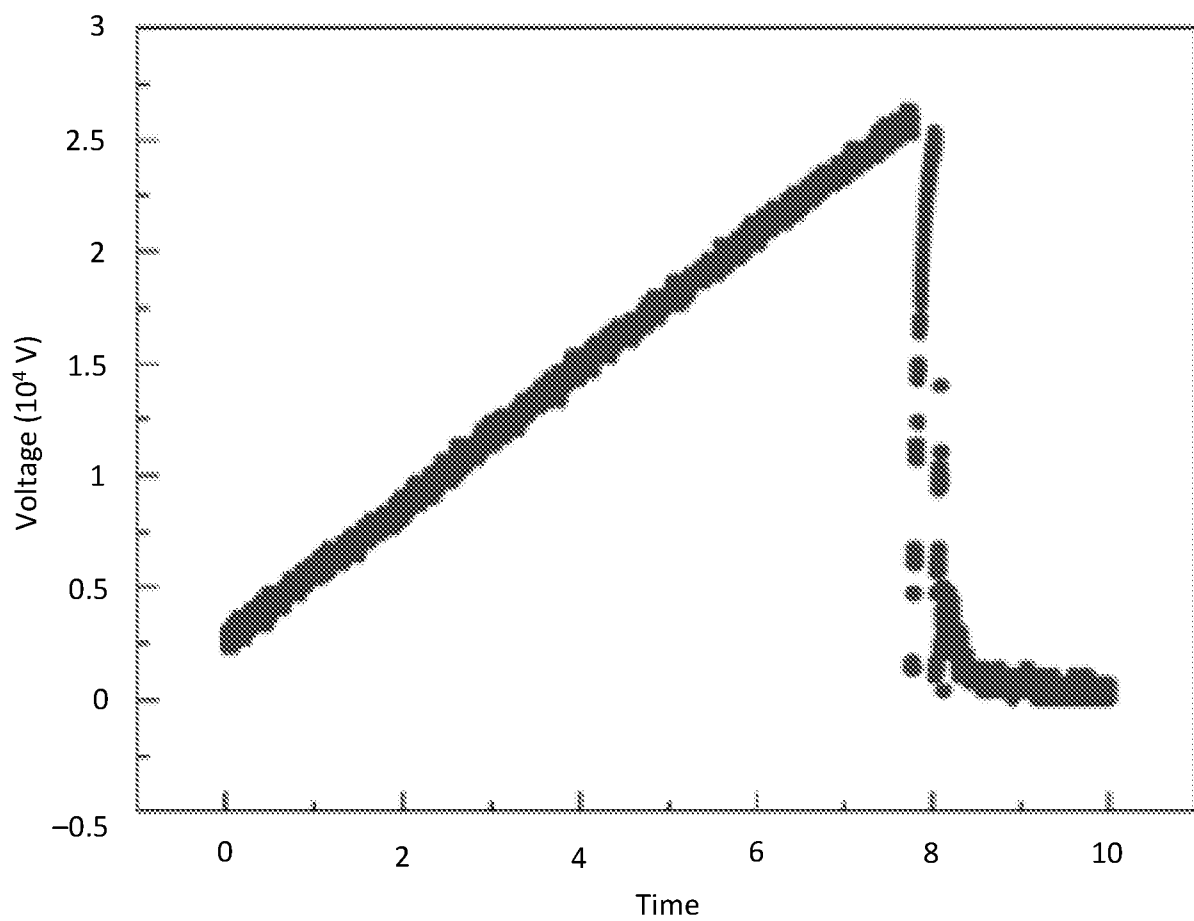
FIG. 4A

FIG. 4B

FIG. 4C

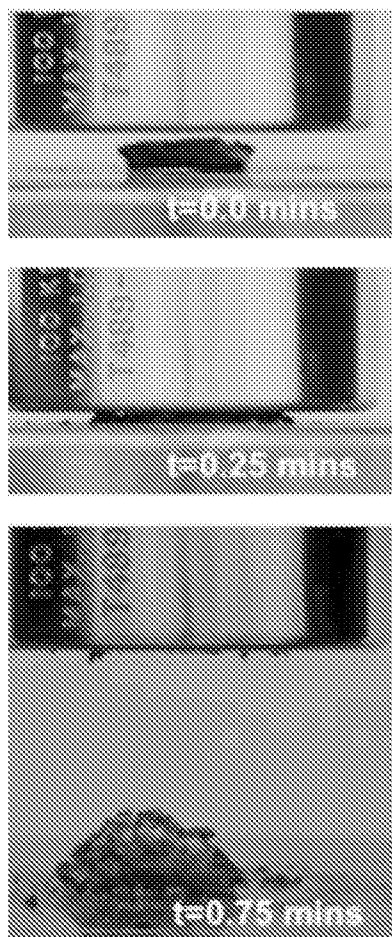
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FIG. 5



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FIG. 6



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/044725

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B19/04 C22C28/00 H01G4/00 H01M4/136
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B H01M H01G C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 201555 Thomson Scientific, London, GB; AN 2015-422387 XP002796645, -& CN 104 617 299 A (SHANDONG YUHUANG CHEM CO LTD) 13 May 2015 (2015-05-13) abstract citations refer to the machine translation into English; paragraphs [0004], [0007], [0008]; claims 1,3 the whole document	1-25
X	CA 911 235 A (XEROX CORP) 3 October 1972 (1972-10-03)	1-22
A	claim 1; figure 2 the whole document	23-25
	----- -/-	



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

3 January 2020

Date of mailing of the international search report

14/01/2020

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/044725

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 712 992 A (SHREEVE NICHOLAS G; LAWES LOUIS F W; MIHALIK NANDOR) 6 July 1965 (1965-07-06) claims 1,3 the whole document	1-25
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2019/044725

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CN 104617299	A	13-05-2015	NONE	
CA 911235	A	03-10-1972	NONE	
CA 712992	A	06-07-1965	NONE	