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Matter of Opinion

Stretchable Ionics: How to Measure the Electrical Resistance/Impedance?

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Abstract

Stretchable ionic conductors have attracted increasing interest in the field of sensors, actuators, bioelectronics and flexible energy devices, due to their high elasticity and biocompatibility. Ionic conductors conduct electrical charges *via* the migration of mobile ions and the "ion-electron" conversion on the electrode interfaces. Therefore, the measurement of electrical resistance or impedance of ionic conductors is normally carried out under AC mode. However, it seems that recent studied ionic devices, especially those "resistive mode" ionic strain sensors, often use DC mode for the characterization. This *Opinion* revisits the conduction mechanism of emerging stretchable ionics and discusses the methods to measure ionic resistance/impedance, aiming to appeal more research attentions on studying the conduction mechanism and characterization protocols for stretchable ionic devices.

Stretchable conductors can be used as circuit connectors, electrodes and active components for flexible devices such as sensors, actuators, and energy storage devices.[1] For example, strain-sensitive conductors can be used to make strain sensors, which work by generating electrical signals in response to mechanical deformations.[2] The most straightforward method to prepare stretchable conductors is to incorporate conductive materials (*e.g.*, metal nanoparticles, carbon nanomaterials, conducting polymers) into/on elastic substrates by methods such as blending, surface coating, and *in-situ* polymerization.[1] The resulting materials are electronic conductors that the electrical conduction is achieved by the transport or tunneling of free electrons or holes. The electrical resistance can be directly measured by applying a direct-current (DC) voltage, and it obeys the Ohm's law. Consequently, a "resistive mode" strain sensor can be assembled by attaching electrodes on the stretchable electronic conductor (***Fig. 1a***). When applying a DC voltage, the cyclic movement of electrons can sustain a continuous conduction (right panel of ***Fig. 1a***), and a resistance change will be induced by an applied strain.

Recently, ionic stretchable conductors have attracted increasing interest for flexible devices owing to their attributes of good stretchability, optical transparency, and biocompatibility.[3] Unlike electronic conductors that employ electrons as the charge carrier, the conduction of ionic conductors is realized based on the migration of mobile ions.[4] Theoretically, when a DC voltage is applied on an ionic conductor, the positive and negative ions, *i.e.*, cations and anions, will migrate oppositely towards the electrodes triggered by the electric field force, and accumulate on the electrode surfaces (***Fig. 1b***). When the applied DC voltage is below the electrochemical window of the ionic matter/solvent and ion-blocking electrodes are used, the output current will decrease quickly and eventually become non-conductive (as illustrated in the right panel of ***Fig. 1b***), due to the depletion of mobile ions or reaching charge equilibrium on the electrodes.[5] Otherwise, to maintain conducting for an extended period of time under DC, the applied voltage needs to exceed the electrochemical window of the ionic electrolyte, or use redox-active electrodes, on which electrochemical reactions will occur. The device in the former case is called an electrolytic cell, and the later one is normally referred as a galvanic cell (battery or fuel cell).

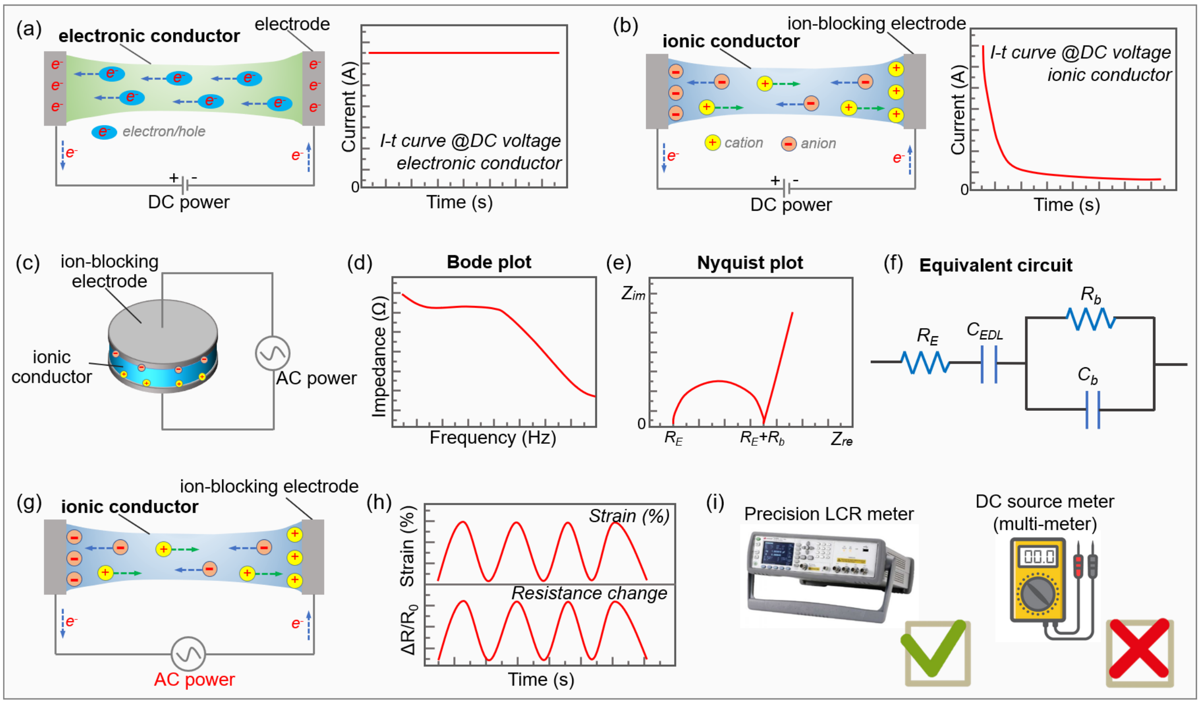

Fig. 1. *(a)* Schematic of the conduction mechanism of electronic conductors that the electrical conduction is maintained by continuous transport of electrons/holes under DC voltage; the right panel shows the corresponding current output characteristics over an extended period of time. *(b)* Schematic (left panel) of the movement of ions in an ionic conductor when applying an DC voltage, and the current output characteristics (right panel) over an extended period of time, showing that the output current decreases quickly and eventually become zero. *(c)* Schematic of the measurement of ionic conductivity by the EIS method. *(d)* Bode plot (impedance *vs.* frequency) and *(e)* Nyquist plot (imaginary impedance (Z_{im}) *vs.* real impedance (Z_{re})) of ionic conductor. *(f)* Equivalent circuit for analyzing the electrical characteristics of the ionic conductor (R_E is the contact resistance of electrodes, C_{DEL} is the electric double layer (EDL) capacitance at the interface of electrodes, R_b and C_b are the bulk resistance and capacitance of the ionic conductor, respectively). *(g)* Schematic of ionic conductor-based strain sensors operating by applying an AC voltage, and *(h)* the general output signal of resistance change ($\Delta R/R_0$) in response to strain change. *(i)* Schematic of testing instruments (precision LCR meter and DC source meter), the precision LCR meter with AC power is suggested for ionic strain sensor testing.

Indeed, ionic conductors widely exist and have been studied enormously in many fields, *e.g.*, ion channels on cell membranes, ion-exchange membranes of fuel cells, and solid-state electrolytes of batteries. With a rapid development of flexible and wearable electronics in the recent years, stretchable ionic conductors have been extensively explored. Ionic conductivity is usually adopted to evaluate the performance of ionic conductors; a higher ionic conductivity represents a fast ion exchange capability. The ionic conductivity is normally measured by the electrochemical impedance spectroscopy (EIS) method. In a typical process, an ionic conductor is sandwiched between two ion-blocking electrodes (*e.g.*, stainless steel, Pt, Au, and Ag foil), and a sinusoidal alternative-current (AC) voltage is applied over a certain frequency range (*e.g.*, 0.1~10^5 Hz) to acquire the impedance data (as illustrated in ***Fig. 1c***). The acquired frequency-dependent impedance data is usually analyzed by transferring to Bode plot (***Fig. 1d***) and Nyquist plot (***Fig. 1e***) and fitting by an equivalent circuit (***Fig. 1f***). The bulk resistance (R_b) of the ionic conductor can be obtained from the semicircle located at the high-frequency range in the Nyquist plot, and the ionic conductivity (σ) can be then calculated by the equation: $\sigma = L/R_bA$ (where L and A are the thickness and area of the ionic conductor, respectively).

Based on the above discussion, an AC voltage is ought to be applied if one want to use the "resistive mode" (***Fig. 1g***), which monitors the resistance change of the ionic strain sensors (***Fig. 1h***), to study the conductance/resistance of the ionic conductor. Consequently, AC power source meters (*e.g.*, precision LCR meter) are required for the measurement, while DC power meters (*e.g.*, multi-meter) are not feasible (***Fig. 1i***). In addition, since AC impedance is frequency-dependent, a specific testing frequency needs to be optimized for the measurement. Therefore, flexible devices based on ionic conductors are generally assembled in operating with capacitive mode, where the ionic conductor is used as a (super)capacitive dielectric layer.[6,7] We notice that a large number of literatures reported the fabrication of "resistive mode" strain sensors using stretchable ionics recently. However, a majority of works adopted the DC method for testing the performance of ionic strain sensors. Such a DC operation mechanism was seldom discussed.

Why can those ionic strain sensors be conductive persistently and work under a DC voltage? The reasons may include the following aspects. First, some non-negligible electronically conductive components are inadvertently introduced into the prepared ionic material, which may come from chemical impurities, tiny particles dropped from metal electrodes, or the filler itself is intrinsically an electronic-ionic mixed conductor (*e.g.,* conducting polymer).[8] Therefore, the resulting ionic conductor has an ohmic leakage current under applying a DC voltage (***Fig. 2a***). Second, ions re-distribution may be induced by applied strain, since the dynamic strain can not only cause mechanical deformations but also change of electrical field. Therefore, the movement of re-distributed mobile ions in the ionic conductor will contribute to a continuous conduction (***Fig. 2b***). Third, some electrochemical redox reactions may occur on the electrodes (***Fig. 2c***). For example, when an ionic hydrogel is applied with a relatively high voltage (> 1.23 V), hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) may occur on the two electrodes, respectively. Even if the applied voltage is low (< 1.0 V), some reactions such as massive adsorption of ions (super-capacitive electrode), dissolution of electrode metals, and other thermodynamically spontaneous reactions may still occur.[9] Moreover, if the electrodes are reversible battery-type materials, it is interesting to assembly a "battery-mode" self-powered ionic strain sensor.[10] These speculations need to be verified in the future study.

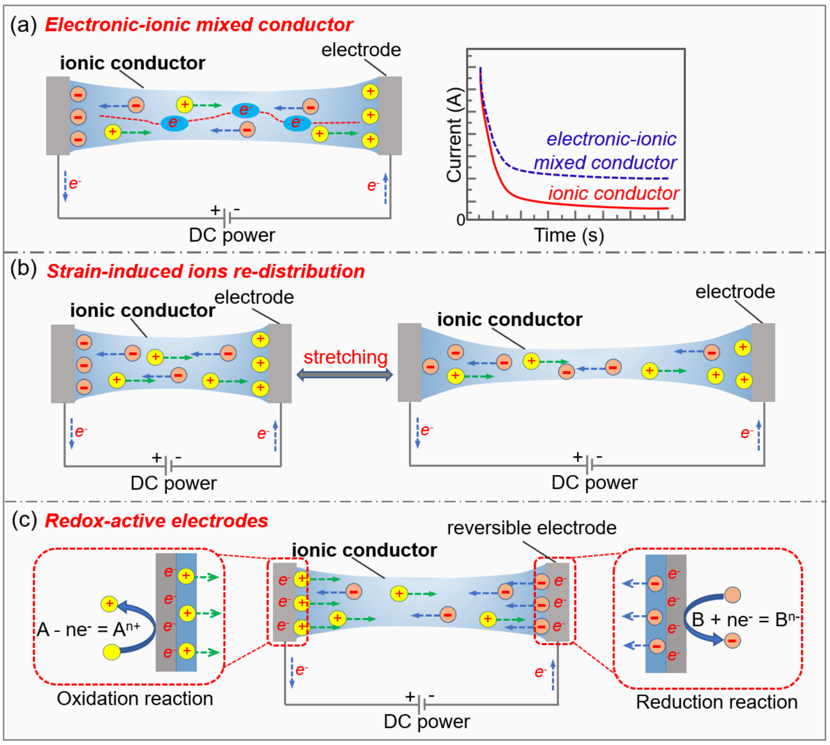

Fig. 2. **Possible reasons for ionic strain sensors can work under DC mode:** *(a)* Electronic-ionic mixed conductor: some electronic impurities are introduced into the ionic conductor that cause an ohmic leakage current, the right panel schematically shows the output current characteristics. *(b)* Strain-induced ions re-distribution: applied dynamic strain will cause deformation and electric field change of the stretchable ionic conductor. *(c)* Redox-active electrodes: some electrochemical redox reactions may occur on the electrodes of an ionic conductor.

In summary, stretchable ionics have emerged as a promising direction of flexible devices, yet the characterization of resistive-mode ionic strain sensors is still promiscuous. We here briefly discussed the conduction mechanism and characterizing methods of ionic conductors. However, more efforts are needed to put into studying stretchable ionics. Ionic conductors used for flexible devices usually have larger size and dimensions than conventional electrolytes, and they are working under dynamic strains. The distribution and migration behavior of ions (particularly under dynamic strain) should be studied. The underneath mechanisms and/or possible causes of currently reported ionic strain sensors can work under DC mode need to be carefully clarified. We find that the resistance of the reported stretchable ionics is relatively low when measured by the EIS method (typically lower than 100 Ω), while it is quite large (higher than 10 kΩ) during sensing test by applying a DC voltage. Due to the high initial resistance (R_0), the sensitivity (gauge factor, $GF=(\Delta R/R_0)/\varepsilon$) of the reported "resistive-mode" ionic strain sensors is generally low (typically $GF<5$). If using AC method for testing, it is anticipated that the sensitivity would be largely improved. Hence, standard protocols for characterization of "resistive-mode" ionic devices need to be established. Based on the discussion, AC method is suggested, and thereinto particular attentions must be taken in selecting electrodes and applying voltage and frequency, *etc*. Overall, it is envisaged that the development of stretchable ionics will be pushed forward by revealing the conduction mechanism and building good experimental practice.

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Biography

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