Quantifying Electronic and Ionic Conductivity Contributions in Carbon/Polyelectrolyte Composite Thin Films

Jamie A. Shetzline* and Stephen E. Creager**

Department of Chemistry, Clemson University, Clemson, South Carolina 29634, USA

A method for independently obtaining electronic and ionic contributions to electrical conductivity in thin-film samples comprised of carbon black (CB) mixed with polymer electrolyte is reported. The method relies upon careful control of the nature of the contact between the sample and the current-carrying electrodes. Electronic conductivities are derived from currents obtained using electronically-conductive glassy carbon electrodes to contact the sample, whereas ionic conductivities are derived from currents obtained using ionically-conductive Nafion electrodes to contact the sample. Conditions under which the measured currents are free from interference from redox reactions at the electrodes and capacitive charging at electrode-electrolyte interfaces are discussed. Electrical conduction was studied in a series of composite carbon black/polymer samples under conditions of fixed temperature and variable relative humidity (RH). For samples containing 10–20 weight percent carbon black dispersed in Nafion, electronic conductivity was higher than ionic conductivity at all RH values tested (25–100% RH). Ionic conductivity increased with increasing RH in a manner consistent with expectation from prior studies on Nafion membranes, whereas electronic conductivity decreased with increasing RH due to water swelling and weakened electrical contacts among carbon particles in the network.

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Electrical conduction in materials may arise from motion in an electric field of electrons, ions, or both. For many materials the charge carrier identity is implicit; e.g. for metals and semimetals such as carbon, charge is understood to be carried by mobile electrons, whereas for electrolyte materials such as salts dissolved in solvents and most polymer electrolytes, charge is understood to be carried by mobile ions.1,2 Some materials have the very interesting property that they may transport charge via both ions and electrons; such materials are referred to as mixed ionic electronic conductors (MIECs).3–5 MIEC materials are critically important in many electrochemical technologies, for example in battery electrodes,6–13 fuel-cell electrodes,14–16 and in certain types of membrane reactor.17–20

A simple measurement of electrical resistance/conductance on a bulk sample, for example from the current obtained upon application of a potential difference between two points on the sample using current-carrying electrodes, can provide values for resistivity/conductivity but it does not provide information on the nature of the charge carrier(s). Four-point-probe (e.g. van der Pauw) measurements are useful for eliminating the influence of contact resistance at the current-carrying electrodes on the measured resistance but such measurements still do not distinguish whether charge is carried by electrons, ions, or both. For some special situations, e.g. doped semiconductors, information about charge-carrier identity may be obtained from the behavior of the sample in response to an external perturbation. For example, in the case of Hall-effect measurements, a magnetic field is applied across a sample through which current flows, and a potential difference develops across the sample in a direction perpendicular to both the direction of current flow and also to the direction of the magnetic field.1 From the magnitude and sign of this potential difference, the sign and mobility of the principal charge carrier (typically electrons or holes) may be obtained. Such measurements can be valuable for some materials but are often not very informative for complex materials that may transport charge using multiple types of charge carrier.

The case of polyelectrolyte membrane (PEM) fuel-cell electrodes is particularly interesting and important. In such electrodes, mixed conduction occurs because the materials are composites, consisting of an electronic conductor such as carbon black (CB) mixed with an ionic conductor, often a polymer electrolyte such as Nafion, in a bicontinuous network. Mixed conduction is needed throughout these electrodes because the electrode reactions always involve generation and consumption of both ions and electrons. High activity is achieved when transport rates are high for both ions and electrons throughout the entire three-dimensional structure of the electrode. Measurement of the electronic and ionic contributions to electrical conductivity in fuel-cell electrodes is therefore very important, but it can also be problematic. Electrochemical impedance methods have been used21–27 to study electrodes in fuel cells but this can be a difficult measurement to make, subject to errors associated with high currents and possible contributions from ohmic and mass-transfer resistances in other parts of the cell besides the electrode. Materials properties derived from electrochemical impedance measurements are also inherently very model-dependent and for composite materials such as PEM fuel-cell electrodes, many assumptions must be made to create an equivalent circuit model that properly accounts for all the things that are happening in the cell, including capacitive charging, electrode kinetics, mass transfer of fuels and oxidants, and bulk electron and ion transport in all parts of the cell. Errors in the assumptions and in the equivalent circuit model will produce errors in determining electrode properties. There have been a few reports on the use of near-DC conditions to measure electronic and ionic conductivities in freestanding thin-film MIEC electrodes.28–31 In some cases, the nature of the contact between the electrodes and the sample is controlled to restrict charge flow to only a certain type of charge carrier. These methods are similar to the Hebb-Wagner method that has long been used to study mixed electronic and ionic conduction in inorganic solids, e.g. silver sulfide in the original work of Hebb.32–36 This approach cannot be easily used on electrodes in an active fuel cell but it is nonetheless useful at the materials discovery stage because it allows for focused study of the variation in electronic and ionic conductivity contributions within electrodes in response to systematic variation of materials parameters and conditions. Such studies could be highly valuable in research aimed at creating new MIEC electrode materials.

We report here on a simple but significant extension of some of this earlier work30,31 for obtaining the separate contributions of electron and ion transport to the electrical conductivity of thin-film samples comprised of carbon black mixed with a polymer electrolyte. The method adapts a commercially available system for measuring in-plane conductivity in thin films to allow for careful control of the nature of the contact between the sample and the current-carrying electrodes. Electronic conductivity is studied by measuring the near-DC current that flows upon application of a small potential difference across the sample using glassy carbon electrodes to contact the sample, whereas ionic conductivity is studied by measuring the current that flows when applying a small potential difference across the sample using contacting electrodes that carry ions but not electrons. These methods are adaptable to practical fuel-cell electrodes.
two cell configurations are illustrated in Figure 1. The latter situation requires some care to create since the electrical connection between the sample and the measurement system must at some point involve an electronic conductor (e.g., a wire) connected to an instrument used to apply potential differences and measure current. We achieve this situation using a stack consisting of a silver metal foil, a Nafion membrane in the silver ion form, and a Nafion membrane in the protonated form. DC current can flow in such a cell when silver ions are reduced at one silver electrode and silver metal is oxidized at the other electrode. Using cells configured in this way, we have made separate measurements of electronic and ionic conductivity for mixtures of carbon black with Nafion (and also with poly(vinylidene difluoride) as a control) under conditions of controlled temperature and relative humidity (RH). For relatively modest carbon contents (10–20 weight percent), we find that electronic conductivity is quite high and relatively invariant with RH. Ionic conductivity is significantly lower, indicating that ion transport is more likely than electron transport to be the factor limiting overall electrical conduction in these electrodes. Variation of electronic and ionic conductivity with RH is consistent with significant absorption of water by the samples at the higher RH conditions.

Electronic and ionic conductivity measurements.— Conductivity measurements were made using the cell illustrated in Figures 1 and 2, which was designed to fit inside of a BekkTech model BT-112 cell that is normally used for making four-point-probe ionic conductivity measurements on polyelectrolyte membrane samples. The cell is coupled to a Scribner Associates model 850C fuel-cell test stand which is used to control the cell temperature and the relative humidity of nitrogen gas passing through the cell. The sample holder is a machined piece of Teflon having wells at each end that are approximately 1 cm on a side and are deep enough to hold the glassy carbon or silver electrodes. Slots were cut to allow for exposure of the sample to the humid gas environment in the cell. This sample holder is illustrated in the photographs in Figure 2. Electrical connection to the glassy carbon and silver electrodes is made via narrow-gauge platinum wire contacts embedded in the bottom of the wells that hold the electrodes. The thin-film sample is placed on top of the electrodes and a second...
slotted Teflon piece is placed on top of the sample and held tight by four screws to ensure firm contact between the sample and the electrodes. For electronic conductivity measurements the glassy carbon electrodes are in direct contact with the thin-film sample, and for ionic conductivity measurements, small pieces (approximately 1 cm²) of Nafion 212 membrane in silver ion form and protonated form are positioned between the silver electrode and the sample, as shown in Figure 1. Electrical measurements were made using a CH Instruments model CHI1100-B potentiostat with the working electrode wire connected to one electrode and the reference and counter electrode wired shorted together and connected to the other electrode. Currents were measured using a cyclic voltammetric DC ramp waveform at a rate of 0.1 mV sec⁻¹, starting at zero volts bias with switching potentials of +10 mV and −10 mV and a quiet-time delay of 200 sec at zero bias before data acquisition began. Values for electrical resistance of samples were calculated from the slope of current vs. voltage curves, and conductivities were calculated from resistance values using the previously measured width and thickness of samples, and the known spacing between electrodes of 2.7 cm. Samples were initially held at a RH value of 70%, then the RH was decreased to approximately 25% then increased to near 100%. RH variation was accomplished by varying the temperature of a sparging bottle for gas that was passed through the cell, while holding the cell temperature constant, according to the instructions for the Scribner model 850C fuel-cell test unit.

Electron microscopy characterization.— Thin-film samples were imaged with a high-resolution scanning electron microscope (SEM, Hitachi model S4800) using an accelerating voltage of 5kV for lower carbon content samples (≤10% CB) and 10kV for higher carbon content samples. Samples were freeze-fractured in liquid nitrogen prior to imaging to expose a cross-sectional surface.

Results and Discussion

As was noted earlier, the method described herein for independently measuring electronic and ionic contributions to electrical conductivity relies upon careful control of the blocking and non-blocking (aka conducting) character of the contacts between the sample and the current-carrying electrodes. Figure 3 presents a set of six slow-scan cyclic voltammograms for three samples that illustrate how this method works. The three samples studied are (a) a PVDF film, expected to have no significant electronic or ionic conductivity; (b) a film comprised of 20 weight percent carbon black in PVDF, expected to have significant electronic conductivity but nearly zero ionic conductivity; and (c) a Nafion 117 membrane, expected to have significant ionic conductivity but nearly zero electronic conductivity. Each sample is subjected to a slow-scan CV over a restricted potential range with one of two types of contact: a pair of glassy carbon electrodes, or, a pair of silver electrodes with films of Nafion in silver and proton forms positioned between the silver metal and the sample. The currents obtained for each sample, in each configuration, reflect contributions to electrical conductivity from electrons and ions, as described below.

Glassy carbon is a good electronic conductor but a very poor ionic conductor, so glassy carbon contacts with the sample are expected to be blocking for ions but non-blocking (conductive) for electrons. Currents through the sample measured in this configuration are expected to show contributions from only electronic conductivity. The data in Figure 3 are consistent with this expectation; Figure 3b for the carbon black/PVDF sample shows significant current in this configuration, whereas Figure 3c for the Nafion samples shows nearly zero current in this configuration. The other contact configuration is more complex, consisting of multiple interfaces, but the end result is that contact is made with the sample via a Nafion membrane in protonated form. Nafion is a good ionic conductor (in the protonated form it is a good proton conductor) but a very poor electronic conductor, therefore Nafion contacts with the sample are expected to be blocking for electrons but non-blocking (i.e., conductive) for ions. The data in Figure 3 are consistent with this expectation. Figure 3b for the carbon black/PVDF sample shows nearly zero current in this configuration, whereas Figure 3c for the Nafion samples shows significant current in this configuration. Currents are very nearly zero in both configurations for the PVDF sample in Figure 3a, as expected for a sample that is expected to contain almost no charger carriers and that should therefore have nearly zero electrical conductivity of any sort.

Resistance values for the samples are easily obtained from the slopes of slow-scan CVs such as those in Figure 3, and those values may be converted to in-plane conductivity by accounting for the sample geometry (sample width and thickness and distance between electrodes) and assuming current flow is homogeneous across the cross-sectional sample area (width times thickness). Figure 4 presents conductivity values obtained in this way for the three samples from Figure 3, in the ion-blocking (glassy carbon) and electron-blocking
Figure 4. Conductivity measurements acquired at 80°C and variable relative humidity using the cell from Figures 1 and 2, configured to measure electronic (circles) and ionic (squares) conductivity for three samples: (a) PVDF (30 μm); (b) 20% Carbon Black + 80% PVDF (18 μm); and (c) Nafion 117 (189 μm). Samples initially started at approximately 70% RH; filled symbols were acquired with decreasing RH, and open figures were acquired with increasing RH.

Figure 5. Electronic (circles) and ionic (squares) conductivities at variable relative humidity for thin-film samples prepared from carbon black mixed with Nafion. (a) 10% carbon black/90% Nafion and (b) 20% carbon black/80% Nafion. Electronic conductivity decreases with increasing relative humidity whereas ionic conductivity increases with increasing relative humidity.

(Nafion) configurations. The data are shown for a fixed temperature but a series of different relative humidity (RH) values for the gas environment surrounding the samples. There are several interesting points to be made regarding Figure 4. First, for the PFDV film sample, conductivity values obtained in electron and ion transporting configurations were consistently between about $10^{-5}$ and $10^{-7}$ S cm$^{-1}$. These numbers probably do not reflect true values of electronic or ionic conductivity for PVDF; rather they reflect the error associated with measuring the slopes of IV traces that have a slope very close to zero. In fact upon close inspection some of the slopes for IV curves with nearly zero slope were found to be negative, and the overall response for the PVDF film was found to be indistinguishable from the response obtained with no sample present. We therefore take the lower limit of detection on conductivity for samples studied in this way to be approximately $10^{-5}$ S cm$^{-1}$.

For the carbon black/PVDF sample the electronic conductivity is relatively high (over 1 S cm$^{-1}$) and nearly invariant with humidity, and the ionic conductivity is relatively low (between $10^{-3}$ and $10^{-5}$ S cm$^{-1}$) and rises modestly with rising humidity. The high electronic conductivity is as expected for a composite material containing an electronic conductor above the percolation threshold, and the weak humidity dependence of the electronic conductivity is as expected for a material that is not expected to absorb water. The low ionic conductivity is also as expected for a material thought to contain no (or very few) ionic charge carriers. In fact, the ionic conductivity values are higher than would have been expected for just PVDF. We speculate that the carbon black samples may contain a small number of mobile ions, perhaps associated with surface functional groups, that upon exposure to moisture are able to contribute to ionic conductivity.

For the Nafion sample, electronic conductivity values between $10^{-5}$ and $10^{-6}$ S cm$^{-1}$ were obtained for nearly all RH values, which is consistent with the values obtained for PVDF and is thought to reflect the lower limit on conductivity which can be reliably measured by this method. Ionic conductivity values were much higher, between $10^{-1}$ and $10^{-3}$ S cm$^{-1}$, and rise significantly with rising RH. These ionic conductivity results are completely in line with expectations from literature reports on Nafion ionic conductivity obtained in a variety of ways under similar conditions.37

Figures 5 and 6 present results on the effect of varying the amount of carbon black in samples on the electronic and ionic conductivity, both as a function of RH at fixed temperature. Figure 5 shows the variation with RH of electronic and ionic conductivity for two carbon black/Nafion composite samples, one containing 10 weight percent...
carbon black (top) and the other containing 20 weight percent carbon black (bottom). Both samples show a trend of increasing ionic conductivity and decreasing electronic conductivity as RH is increased. The trend of increasing ionic conductivity with increasing RH is expected for samples that consist mostly of Nafion ionomer; increasing RH causes increased water uptake and proton solvation, thereby allowing for increased proton diffusion/mobility and higher ionic conductivity even as proton concentrations slightly decrease due to dilution by the water. The cause for decreasing electronic conductivity with increasing RH is also understood as a consequence of water uptake; as the sample absorbs more water it swells, which weakens the electrical connections among carbon black particles within the percolated carbon black network.38 Similar effects are seen by mechanically stretching composite materials containing carbon black, or by absorbing gases into composite films of carbon black and various soft hydrophobic polymers such as rubber (e.g. the “electronic nose”).39

Figure 6 presents data on just electronic conductivity, for fixed temperature and RH conditions, for a series of carbon black/polymer samples as a function of weight percent of carbon black in samples where the polymer is PVDF (solid circles) and Nafion (half-solid circles). Electronic conductivity for carbon contents below about 2% is indistinguishable from that of samples containing no carbon. For carbon contents of 5% or above, both sample series show increasing electronic conductivity with increasing carbon content, but the conductivity decrease is not simply proportional to the amount of carbon, e.g., increasing carbon content from 10 to 20 percent causes conductivity in both samples to increase by almost 10X. This behavior is as expected for samples in which electronic conduction occurs along a percolated network, at a composition close to the percolation threshold.38,40,41 Close inspection of the data for samples at 10 and 20 weight percent carbon reveals that, for the same carbon content, electronic conduction is consistently lower for samples made from Nafion than for samples made from PVDF. There could be many reasons for this difference including differing degrees of carbon aggregation in the samples, and differences in polymer coating of individual carbon black particles for the two polymers. The carbon/Nafion samples are also expected to absorb significantly more water than the carbon/PVDF samples, which as discussed above will result in an overall sample expansion and a weakening of the carbon-carbon electrical contacts. Also, as will be discussed below, these carbon black/polymer composites all contain significant amounts of free volume which further complicates simple comparisons of conductivity among samples. Additional work would be required to provide better answers to these interesting mechanistic questions regarding why electronic and ionic conductivity vary as they do with sample composition and RH for these samples.

Figure 7 shows cross-sectional SEM images of an electronically conductive CB/PVDF composite and a mixed conducting CB/Nafion composite, each containing 10% by weight carbon black. Both images show aggregates of carbon black in a size range between approximately 50 and 200 nm, dispersed within a polymer matrix. Carbon particles are clearly in contact with each other but it would be difficult to say from just these images whether the aggregation was greater for the Nafion or PVDF samples.

The images in Figure 7 also suggest that both samples contain relatively large amounts of void space. This sample attribute may be further understood via simple macroscopic density calculations on the thin-film samples, obtained from the mass and the approximate length, width and thickness of samples. Estimates of sample density obtained in this way are provided in Table I. Density estimates for commercially-obtained membranes of Nafion and PVDF (first two entries in Table I) agree with literature values (1.76–1.78 g/cm3 for PVDF and 1.8–2.0 g/cm3 for Nafion, depending upon source and pretreatment)13 to within ten percent, however the measured densities for solvent-cast films of PVDF and Nafion (second two entries in Table I) are lower, and those for both of the composite samples (last two entries) are much lower, well below 1.0 g/cm3. Calculated densities listed in Table I for the composite samples are obtained assuming no free volume and an amorphous carbon density of 2.0 g cm−3. If the
discrepancy between the calculated and measured densities is assumed to be due solely to void space in composite samples, we may readily estimate that both of the composite samples are comprised of 70–75% void space by volume. Gravimetric water uptake and the associated dimensional swelling by samples containing Nafion is also much greater for the Nafion-carbon composite than for dense Nafion membranes. This finding probably reflects the large amount of void space, perhaps coupled with a diminished mechanical strength, for the composite samples compared with dense Nafion films. These facts will certainly affect the variation of conductivity with composition and humidity in the composite samples.

It is instructive to compare the ionic conductivity of Nafion in a Nafion/carbon black composite with that of a Nafion film without additives. Figure 8 presents such a comparison, showing plots of ionic conductivity vs. RH for two samples, one a Nafion film prepared by solvent casting, and the other a Nafion sample containing 20% carbon black, also prepared by solvent casting. These two samples correspond to entries MC10 and MC120 in Table I. There are two significant points to be made about the data in Figure 8. First, ionic conductivity of the Nafion/carbon black sample is higher at all RH values than that of the Nafion sample not containing carbon black; and second, ionic conductivity decreases for both samples with decreasing RH but the decrease is greater for the MC10 sample than for the MC120 sample. These findings could reflect many factors including the tendency of the composite samples to absorb and retain water more strongly than Nafion alone, and possibly a change in ionomer morphology (change in size/shape/orientation of ionically-conductive domains) when carbon black is present. We note that similar effects on ionic conductivity have been seen for Nafion samples containing insulating inorganic oxides as additives. These findings suggest that further studies designed to focus on the both the structural changes in the ionomers and the membranes, and the changes in electronic and ionic conductivity that occur in composite samples as a function of RH as they take up and lose water, would be informative.

It is useful to consider the possible roles that contact resistance, redox reactions, and capacitive charging could play in affecting cell currents. The ohmic current through a sample at a fixed applied potential reflects all resistances in the path of current flow including resistance of the contact between the electrode and the sample. We have used a cell geometry in which the contact area is quite large, the sample thickness is small and the spacing between the two electrodes is large. The pressure forcing the electrodes to contact the sample is kept high, and the sample is relatively compliant so that contact between the sample and the electrodes is likely to occur over their full area. These conditions are all intentionally created to ensure that contact resistance does not significantly contribute to the overall cell resistance. Evidence that this is the case is provided in some preliminary studies on samples of variable length and width; cell currents vary systematically in proportion to these changes in cell geometry in a manner expected for the geometric changes (e.g. doubling the sample length or halving the sample width causes current to diminish by half), which indicates that the currents are limited principally by sample resistance and not contact resistance.

Regarding the possible role of electrochemical oxidation/reduction reactions at the sample/electrode contact, voltammetric scans were intentionally limited to a very small potential range such that electrode reactions such as oxidation/reduction of protons, water, or other species that might be present at the interface would not occur. Evidence that such reactions do not occur is provided by the high linearity and the steady-state character of the voltammograms. If oxidation/reduction reactions were occurring at the scan limits, current would be expected to rise non-linearly with application of increasingly positive or negative potentials and to vary significantly with time, as a result of the mixed control of current by electrode kinetics and concentration polarization for the reactants and products. In fact, under the conditions we have selected, current-voltage curves were always observed to be highly linear and steady-state in character, suggesting that they are not influenced by any unexpected electrode reactions.

Capacitive charging is always a possible source of current flow in cells where electronic and ionic conductors are in contact with each other and where the electrochemical potential applied to the conductor is changing. Capacitive charging is however inherently time-dependent; if enough time is allowed to pass following a step change in applied potential, charging currents will eventually diminish to be very close to zero, and if the applied potential is changed sufficiently slowly, the currents required to continually charge the interface capacitance will become quite small. It is for this reason that we have used extremely low scan rates (0.1 mV s⁻¹) to acquire the voltammograms in our experiments. Slow scanning results in low currents for capacitive charging yet still allows for near-DC currents to pass which are the result of charge carriers moving through the sample in ohmic fashion. Evidence that the currents passing in our cells are from bulk charge-carrier transport and not capacitive charging is provided by the

| Table I. Density and water uptake for samples of carbon black in Nafion and PVDF. |
| Sample | Composition | Measured density g cm⁻³ | Calculated density g cm⁻³ | Water uptake weight% | Water swelling volume% |
|--------|-------------|-------------------------|---------------------------|----------------------|-----------------------|
| PVDF   | 100% PVDF   | 1.61                    | 1.76–1.78                 | ~0                   | ~0                    |
| Naf117 | 100% Nafion | 1.88                    | 1.8–2.0                   | 31                   | 38                    |
| EC10   | 100% PVDF cast | 1.29                | 1.76–1.78                 | ~0                   | ~0                    |
| MC10   | 100% Nafion cast | 1.35                | 1.8–2.0                   | 42                   | 39                    |
| EC120  | 20%CB/80%PVDF | 0.44                  | 1.86                      | 11                   | 16                    |
| MC120  | 20%CB/80%Naf | 0.60                    | 1.96                      | 125                  | 124                   |

Figure 8. Ionic conductivity vs. RH for membrane sample MC120 containing 20% carbon black in Nafion (triangles) and for sample MC10 containing only Nafion, with no carbon black (squares). Both membrane samples were prepared by a similar solvent casting procedure as described in the experimental section.
near-invariance of current that we observe with variations in scan rate (data not shown).

Finally, we note some similarity between our approach and an approach recently described by Siroma and co-workers involving four electrodes contacting a sample (two electronic conductors and two ionic conductors) and two independent potentiostats. The method of Siroma has the advantage that it can provide ionic and electronic conductivities from a single experiment, by separately measuring current that flows through the sample through the electronically and ionically conductive electrodes. A disadvantage of their method is that it requires the use of two independent potentiostats and six electrodes (counting reference electrodes) in simultaneous contact with the sample. The present method provides similar information to the method of Siroma but uses only one potentiostat and requires only two contacts with the sample. The present method is simpler to apply and may be more generally applicable to a wider range of samples than the approach described by Siroma.

Conclusions

In conclusion, we report on a method for independently obtaining the electronic and ionic contributions to electrical conductivity in samples comprised of mixtures of carbon black (an electronic conductor) and Nafion (an ionic conductor). Variation of both contributions to conductivity was studied with respect to variations in carbon content and relative humidity. By careful consideration of the contacts between the sample and the current-carrying electrodes and on the conditions used to apply potentials and measure currents, it has been possible to focus on ohmic currents due to just one type of charge carrier. It will be interesting to see how the method could be extended to include other types of MIEC materials, for example materials in which more than one type of ion can contribute to ionic conduction, and on materials where the structural morphology of interpenetrating networks for electron and ion conduction are systematically varied.

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