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► **To cite this version:**

J.-C. Badot, E. Panabiere, N. Emery, Olivier Dubrunfaut, S. Bach, et al.. Percolation behaviors of ionic and electronic transfers in $\text{Li}_{3-2x}\text{Co}_x\text{N}$. *Physical Chemistry Chemical Physics*, 2019, 21 (5), pp.2790-2803. 10.1039/C8CP06770H . hal-02089948

HAL Id: hal-02089948

<https://hal.science/hal-02089948v1>

Submitted on 15 Jul 2021

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Percolation behaviors of ionic and electronic transfers in $\text{Li}_{3-2x}\text{Co}_x\text{N}$

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Key words: Broadband Dielectric Spectroscopy; Lithium nitridocobaltate; Percolation; ionic and electronic conductivity

Abstract

Nitridocobaltates $\text{Li}_{3-2x}\text{Co}_x\text{N}$, with Li_3N -type layered structure, are promising compounds as negative electrode materials for Li-ion batteries. In the present paper, we report the first detailed broadband dielectric spectroscopy (BDS) study on lithiated transition metal nitrides. Ionic and electronic conductivities of $\text{Li}_{3-2x}\text{Co}_x\Box_x\text{N}$ compounds ($0 \leq x \leq 0.44$) are investigated as a function of the concentration x of cobalt ions, cationic vacancies (\Box) and lithium ions. Dielectric and conductivity spectra were recorded within the frequency range $60 - 10^{10}$ Hz from 200 to 300 K. Experimental results exhibit two types of electric conduction: the first one is due to lithium ion diffusion (for $0 \leq x \leq 0.25$) and the second one to electronic transfers (for $x \geq 0.3$). Furthermore, two percolation transitions are evidenced and associated with 3D ionic transfers (threshold at $x \approx 0.11$) on the one hand and 2D electronic transfers (threshold at $x \approx 0.30$) on the other hand. By increasing the frequency, dielectric relaxations appear from larger to smaller sample scales. These successive polarizations appear with increasing frequency according to the following order: (a) sample/silver paint interface; (b) particles (aggregates of grains); (c) grains (crystallites); (d) local ionic and electronic motions within the grains. Evolutions of dielectric relaxation parameters (dielectric strength and relaxation frequency) with Co content confirm the two percolation transitions. Surprisingly, the grain conductivity has a large discontinuity immediately below the electronic percolation threshold where any local- and long-range ionic movement disappears without electronic transfer. This discontinuity would be due to a narrow transition from ionic to electronic conduction when x increases.

1 **1. Introduction**

2 In the last few years, various transition metal compounds in Group V (nitrides [1,2],
3 phosphides [3,4] and antimonides [5,6]) have been investigated as negative electrode
4 materials according to either conversion or insertion reactions for Li-ion batteries. Among
5 nitrides, ternary lamellar compounds with general formula $\text{Li}_{3-x}\text{M}_x\text{N}$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}$) and 3D
6 antiferrotype-type compounds such as Li_7MnN_4 or Li_3FeN_2 have attracted great interest due to
7 their reversible Li insertion properties [1,2,7,8,9,10,11,12]. After pioneering works by
8 Japanese groups showing the potential interest of 2D-nitrides through conversion reactions
9 [13,14], we have recently deeply reinvestigated the structural and electrochemical properties
10 of Li-Co-N and Li-Ni-N systems. These compounds were identified as the most promising
11 2D-nitrides [15,16,17,18]. Nitridocobaltates compounds, obtained using a solid state route
12 from various mixture of Li_3N and Co metal heat-treated at 700°C in a nitrogen gas stream
13 have a general formula $\text{Li}_{3-2x}\text{Co}_x\Box_x\text{N}$ ($0 \leq x \leq 0.44$). In this solid-solution system, an
14 equivalent amount x of Co^{2+} ions and lithium vacancies \Box , leads to a smooth and continuous
15 evolution of the cell parameters versus the cobalt content, according to the Vegard's law
16 [16,19]. Also, in the reduced potential window 0.02-1V vs Li^+/Li , our group demonstrated
17 that these materials are also the first example of intercalation compounds based on a layered
18 nitrogen framework [16,17]. An excellent cycle life is achieved with a stable specific capacity
19 of 180 mAh g^{-1} at C/5 for $\text{Li}_{2.12}\text{Co}_{0.44}\Box_{0.44}\text{N}$. Its electrochemical fingerprint is characterized by
20 a single step around 0.6 V, consistent with the Co^{2+} ions content and a lithium
21 accommodation occurring in the cationic vacancies (\Box) located in Li_2N^- layers. As a
22 consequence, from a structural point of view, the hexagonal layered structure is maintained
23 with a negligible strain limited to a volume expansion of only 1% upon the discharge-charge
24 process. This mechanism explains the excellent cycling life of these $\text{Li}_{3-2x}\text{Co}_x\Box_x\text{N}$ ($0 \leq x \leq$
25 0.44) nitrides where the $\text{Co}^{2+}/\text{Co}^+$ redox couple, lithium ions and cationic vacancies govern

26 the electrochemical features. Therefore, a better knowledge of electronic and ionic transports
27 would help to understand their physical properties.

28 Due to the widely different time scales related to ionic and electronic diffusion in electrode
29 materials, electrochemical methods are appropriate to characterize ionic diffusion properties
30 while electron motion properties cannot be described with these techniques. Conversely, the
31 broadband dielectric spectroscopy from a few Hz to microwave frequencies (a few GHz) is a
32 powerful technique allowing the electrical parameters like permittivity, resistivity and
33 conductivity to be determined as a function of frequency. Such a spectroscopy has been
34 already applied to a multiscale description of electronic transport in various cathode materials
35 for Li-ion batteries like Li_xMoO_3 , Li_xFePO_4 , $\text{Li}_{1+x}\text{V}_3\text{O}_8$ composite electrodes [20,21,22,23].
36 These previous papers have shown that the BDS data cannot be analyzed and interpreted
37 without a thorough knowledge of the material under study (composition, crystal structure,
38 microstructure,...).

39 Li_3N exhibits a layered structure and is well-known for its ionic conductivity within
40 the Li_2N planes, with a conductivity value of $\sigma = 10^{-1} \text{ S m}^{-1}$ [24,25]. Considering the $\text{Li}_{3-2x}\text{Co}_x\text{N}$
41 solid-solution system, with the same layered host lattice than Li_3N , remarkable
42 properties of ionic conduction are expected. Indeed, the increasing amount of lithium
43 vacancies with the cobalt content is expected to be favorable to the ionic conductivity while
44 the introduction of cobalt ions in the structure is favorable to a better electronic conduction,
45 eventually by localized electrons movements through these compounds.

46 In the present paper, we report the first detailed BDS study on transition metal nitrides
47 to investigate ionic and electronic conductivities in the solid-solution system $\text{Li}_{3-2x}\text{Co}_x\text{N}$ ($0 <$
48 $x < 0.44$) as a function of the Co ions, cationic vacancies and lithium ions concentration.

49

50 **2. Experimental**

51 **2.1. Synthesis and structure**

52 $\text{Li}_{3-2x}\text{Co}_x\text{N}$ samples were synthesized through a solid-state route under nitrogen flux. To
53 prepare various compositions of the solid solution $\text{Li}_{3-2x}\text{Co}_x\text{N}$, several mixtures of Li_3N and
54 Co powders were thoroughly ground in an agate mortar and then pressed into pellets. The
55 pellet of about 1 g was then transferred in an alumina crucible enclosed in a tubular stainless
56 steel reactor and heated during 8 h at 720°C under a nitrogen gas stream. A second alumina
57 boat filled with titanium sponge was also added to trap any oxygen and moisture traces
58 present in the gas. All manipulations were carried out in an argon glove box. The Li_3N sample
59 is obtained after a thermal treatment under nitrogen of a pellet made with commercial Li_3N
60 powder. This step is mandatory to have a straight comparison with samples of the Co-
61 contained solid-solution system since the commercial powder contains the two structural
62 polymorphs (α and β) of Li_3N . After the annealing at 720°C under nitrogen gas stream, only
63 the α polymorph (P6/mmm space group) is obtain. X-ray diffraction patterns of the as
64 prepared powder were performed using a Panalytical X'pert pro diffractometer equipped with
65 a Co $K\alpha$ source and an X'celerator detector. Due to the air sensitive character of these
66 nitrides, a polymer airtight sample holder was used.

67 **2.2. Broadband dielectric spectroscopy**

68 Complex permittivity and conductivity of $\text{Li}_{3-2x}\text{Co}_x\text{N}$ samples were measured by the
69 broadband dielectric spectroscopy (hereafter called BDS) from 60 to 10^{10} Hz, using
70 simultaneously a network analyzer Agilent PNA E8364B (10^7 to 10^{10} Hz), two impedance
71 analyzers Agilent 4294 (60 to 1.1×10^8 Hz) and Agilent 4291 (10^6 to 1.8×10^9 Hz). The
72 experimental device consists of a coaxial cell (APC7 standard), in which the cylindrically
73 shaped sample (metallized powder pellet with diameter = 3 mm and thickness \approx 1 mm) fills
74 the gap between the inner conductor and a short-circuit [20,21,26] (Figure S1). After a

75 relevant calibration of the analyzers, the sample admittance Y_s is measured. The knowledge of
 76 Y_s allows determining the complex (relative) permittivity $\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ of the sample,
 77 which enables the calculation of the complex resistivity $\rho(\omega) = [i\omega\epsilon_0\epsilon(\omega)]^{-1}$ (ϵ_0 being the
 78 vacuum permittivity) and conductivity $\sigma(\omega) = [\rho(\omega)]^{-1}$ whose real part $\sigma'(\omega)$ will be hereafter
 79 called the frequency dependent conductivity. Before the measurements of the sample, a
 80 calibration process is applied to remove the systematic errors of the analyzers and coaxial
 81 guide. Complete dielectric spectra have been made from about 600 measurements with an
 82 accuracy of approximately 3 to 5%.

83 **3. Results and discussion**

84 **3.1. Structure and microstructure**

85 XRD patterns of $\text{Li}_{3-2x}\text{Co}_x\text{N}$ samples are displayed in Fig. 1a and 1b. These data can
 86 be easily indexed using a hexagonal structure isotype of $\alpha\text{-Li}_3\text{N}$ (space group P6/mmm) and
 87 all the cell parameters are gathered in Fig. 1c and Table 1. Such a structure (Fig. 1d) can be
 88 simply described by a hexagonal nitrogen network where N^{3-} ions (*1a* site) are surrounded by
 89 6 Li^+ ions (*2c* site), forming Li_2N^- layers. A Li^+ layer (*1b* site) separates these layers. Finally,
 90 N^{3-} ions are arranged in the center of edged sharing hexagonal bipyramids of Li^+ ions. When
 91 Co^{2+} ions substitute a fraction of Li^+ , it occupies the *1b* site, i.e. the cationic interlayer plane
 92 and an equivalent amount of vacancies is created in the *2c* plane, i.e. in the Li_2N^- plane.
 93 Lithium ions of *1b* and *2c* sites will be hereafter called $\text{Li}^+(1b)$ and $\text{Li}^+(2c)$, respectively. The
 94 partial substitution of lithium by cobalt induces changes in electrostatic interaction between
 95 plans. Indeed, the integration of Co^{2+} in the pure Li^+ layer increases its overall positive charge
 96 while the creation of cationic vacancies in the Li_2N^- plane rises the global negative charge.
 97 Consequently, the interlayer distance that is directly related to the *c* axis parameter, decreases
 98 linearly with the augmentation of Co^{2+} content, from $c = 3.876(8)$ Å for Li_3N to $c = 3.625(7)$
 99 Å for $\text{Li}_{2.12}\text{Co}_{0.44}\text{N}$ (Fig. 1c). The *a* parameter gradually increases with the cobalt content, from a

100 = 3.667(7) Å for Li_3N to $a = 3.730(7)$ Å for $\text{Li}_{2.12}\text{Co}_{0.44}\text{N}$, probably due to the progressive
101 reduction of the screening effect of lithium ions between neighboring nitrogen ions. As a
102 result, $\text{Li}_{3-2x}\text{Co}_x\text{N}$ compounds follow the Vegard's law since a and c parameters vary linearly
103 with cobalt substitution (Fig. 1c). Cells parameters of Li_3N and of $\text{Li}_{2.12}\text{Co}_{0.44}\text{N}$ well agreed
104 with previous reports (ref [27,28] and [16,29] respectively). Despite all the precautions taken
105 during the synthesis procedure, a small Li_2O impurity is present on XRD patterns. However,
106 due to the selective character of the BDS and the insulating nature of the Li_2O , the impurity
107 does not affect the measurements.

108 Scanning Electron Microscopy (SEM) micrograph (Fig. 1e) shows the microstructure
109 of the powder, which is constituted of large aggregates with an average size of about 15 to 20
110 μm . Furthermore, the aggregates are made of smaller particles (or grains) with an average size
111 of about 1 to 3 μm (Fig. 1e).

112 3.2. Conductivity and permittivity: long-range and local ionic and electronic motions

113 Conductivity and permittivity spectra (ϵ' and σ' vs. frequency ν) of the different
114 samples at room temperature are shown in Figure 2. Whatever the sample and the temperature
115 in the 200-300 K range, the real part of the conductivity σ' (Fig. 2a) increases up to more than
116 five orders of magnitude over the frequency range 60 to 10^{10} Hz. On the contrary, related real
117 parts of the permittivity ϵ' (Fig. 2b) decrease by about four orders of magnitude in the same
118 frequency range. Also, real parts ϵ' and σ' are highly dependent on the cobalt content x and
119 show several knocks due to various dielectric relaxations. Nevertheless, the frequency-
120 dependent representation does not permit to distinguish easily these different relaxations. The
121 complex plane representation (Nyquist plot) is more convenient to decompose the electric
122 spectra into different contributions.

123 Nyquist plots of the complex resistivity (or impedance) are better adapted to the
 124 determination of the resistivity and the conductivity at the different scales of the materials
 125 (sample, aggregates of grains, and grains within the aggregates). Samples complex resistivity
 126 is generally described by series combination of impedances, each one being parallel
 127 combination of a capacitor and a resistor related to the effective permittivity and conductivity
 128 at a given scale of the material. Hence, the total resistivity of a conducting material is the sum
 129 of various contributions (relaxation functions) given by Equation 1 [30]:

$$130 \quad \rho(\omega) = \rho_g + \left[\sum_m \frac{\Delta\rho_m}{1 + (i\omega\tau_{\rho m})^{1-\alpha_m}} \right] \quad (1)$$

131 where $\omega = 2\pi\nu$ is the angular frequency (in s^{-1}) and ρ_g the intrinsic dc-resistivity
 132 (inverse of the dc conductivity σ_g) of the grain. The term in brackets of Eq. 1 is the sum of the
 133 complex resistivities associated to each scale of the sample from macroscopic to interatomic
 134 size. $\Delta\rho_m$ corresponds to the resistance of each junction (silver paste/sample,
 135 aggregate/aggregate and grain/grain) of the sample, τ_m is a mean relaxation time and α_m a
 136 fitting parameter ($0 \leq \alpha_m \leq 1$). Equation 1 is valid only at the frequencies for which the real
 137 part of $\rho(\omega)$ is higher than ρ_g (dc-resistivity of the grain). In this condition, low and high
 138 frequency parts of $\rho(\omega)$ have the same origin since they are due to charge transfers at the
 139 different scales of the materials (sample, aggregates of grains, and grains within the
 140 aggregates). In Nyquist plot representation, each component is plotted by a circular arc more
 141 or less centered below the ρ' axis. This representation aims at determining the intrinsic grain
 142 resistivity ρ_g and the conductivity σ_g . Since the impedances at different scales are additive (cf.
 143 Eq. 1), their contributions are obtained by a decomposition procedure of the resistivity
 144 spectra. In some cases, Nyquist plots of conductivity are more suitable, if the decomposition
 145 procedure of the spectra into different components is not easy from complex resistivity plots.
 146 Validity of Equation 1 is limited to the frequency range where the real part of $\rho(\omega)$ is higher

147 than ρ_g (dc-resistivity of the grain). In this condition, low and high frequency parts of $\rho(\omega)$ are
148 the same origin since they are due to charge transfers at the different scales of the materials
149 (sample, aggregates of grains, and grains within the aggregates). However, local mechanisms
150 (electronic and ionic local motions within the grain), which occur at the high-frequency part
151 of the spectrum, are analyzed more precisely using Nyquist plots of complex permittivity. The
152 Nyquist plots of complex resistivity for $\text{Li}_{2.76}\text{Co}_{0.12}\text{N}$ and $\text{Li}_{2.22}\text{Co}_{0.39}\text{N}$ at room temperature
153 are shown in Fig. 3a and b, respectively. First, two relaxations R1 and R2 are evidenced. The
154 high frequency contribution R2 is determined by subtracting the low frequency contribution
155 R1 of the total resistivity. The R1 relaxation results in the existence of inter-particle contact
156 resistances and capacitances. The R2 relaxation is thus due to contact resistances and
157 capacitances at grain (crystallite) boundaries inside the particles (aggregates). The high
158 frequency part of R2 crosses the ρ' axis at $\rho' = \sigma_g^{-1}$ where σ_g is the conductivity of the grain
159 or crystallite. Moreover, an additional contribution occurs at frequencies lower than 10^3 Hz
160 for $\text{Li}_{2.76}\text{Co}_{0.12}\text{N}$ (Fig. 3a). The latter corresponds to the contact resistance and capacitance of
161 the interface between the sample and silver metallization. This phenomenon is typical of a
162 metal/ionic conductor junction, giving rise to ionic double-layer at the sample surface. As
163 shown in Fig. S2, conductivity Nyquist plots have been used to determine precisely grain
164 conductivities of Li_3N , $\text{Li}_{2.90}\text{Co}_{0.05}\text{N}$ and $\text{Li}_{2.64}\text{Co}_{0.18}\text{N}$. The different values of the grain
165 conductivities at room temperature are summarized in Table 2. Fig.4 plots the grain
166 conductivity σ_g in function of x (i.e. molar contents of lithium vacancies and Cobalt) at room
167 temperature. The grain conductivity σ_g evolution presents a large discontinuity with a drop of
168 a factor 4 when x varies from 0.25 to 0.32. Also, two well-separated conductivity regimes are
169 thus evidenced in Fig. 4 and due to two types of charge carriers (lithium ions and electrons).
170 They are associated with ionic transfers for lower cobalt contents ($0 \leq x \leq 0.25$) and to
171 electronic transfers for higher cobalt contents (for $0.32 \leq x \leq 0.44$). Electronic transfer only

172 occurs in a 2D continuous network of cobalt ions between Co ions. This finding suggests the
 173 presence of a small amount of Co^+ ions. Evolutions of ionic and electronic conductivities with
 174 the temperature provide information on the activation energies of both types of conductivity.
 175 Indeed, as demonstrated theoretically, the temperature dependence of ionic conductivity σ_{gi} is
 176 given by:

$$177 \quad \sigma_{gi} = \frac{A}{T} \exp\left(-\frac{E_{gi}}{kT}\right) \quad (5)$$

178 as shown in Fig. 5a for $x = 0, 0.05, 0.12, 0.18$ and 0.25 . A is a conductivity prefactor, T the
 179 temperature, k the Boltzmann constant and E_{gi} the activation energy with values between 0.19
 180 and 0.21 eV (see Table 2). For localized electron system like ionic compounds, electronic
 181 transport is usually given by [31,32]

$$182 \quad \sigma_{ge} = \sigma_{0e} \exp\left(-\frac{E_{ge}}{kT}\right) \quad (6)$$

183 as shown in Fig. 5b for $x = 0.32, 0.39$ and 0.44 . The activation energy is $E_{ge} = E_m - E_F$, where
 184 E_m and E_F are the mobility edge energy (bottom of the conduction band) and the energy at
 185 Fermi level, respectively. σ_{0e} is the conductivity prefactor (local conductivity), E_{ge} the
 186 activation energy with values between 0.19 and 0.23 eV (see Table 2). σ_{0e} is not temperature
 187 dependent since electrons move by means of transitions between nearest neighbor cobalt ions.
 188 Then their local mobility follows the Einstein relation [32],

$$189 \quad \mu \propto \frac{ea^2}{kT} 2\pi\nu_t \quad (7)$$

190 where ν_t is the transfer frequency (independent of the temperature) between nearest neighbors
 191 cobalt ions, e the electron charge and a the distance between them. The local conductivity σ_{0e}
 192 is defined as the product of the density of states by the mobility m . Consequently, σ_{0e} is
 193 temperature independent since the density of states is proportional to kT in 2D
 194 semiconductors, which confirm the Arrhenius plot of Fig 5b. Previous work on
 195 $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ exhibits a similar character [33]. **In summary, the activation energies of**

196 ionic and electronic conductivities of the grain are similar, because lithium cations and
 197 electrons would feel the same Coulombic interactions within the crystal lattice.

198 Nyquist plots of the complex permittivity distinguish the responses of the electric
 199 polarizations within the samples. It allows to determine their relaxation strengths and
 200 frequencies related to both charge mobility and to the existence of interfaces at the different
 201 levels of the samples. The interfaces give rise to space-charge relaxations in the lower
 202 frequency range of dielectric spectra. On the other hand, relaxations due to fast local charge
 203 motions are often observed in the higher frequency range of the same spectra. In the
 204 considered frequency range, the frequency dependent complex permittivity is generally given
 205 by:

$$206 \quad \varepsilon(\omega) = \varepsilon_{lat} + \left\{ \sum_j \frac{\Delta\varepsilon_j}{[1+(i\omega\tau_j)^{1-\alpha_j}]^{\beta_j}} \right\} + A(i\omega)^{s-1} + \frac{\sigma_s}{i\omega\varepsilon_0} \quad (7)$$

207 where ε_{lat} is the lattice permittivity of the grain (crystallite), σ_s the dc-conductivity of the
 208 sample, $\varepsilon_0 = 8.842 \times 10^{-12}$ F.m⁻¹ the vacuum permittivity, and s an empirical parameter ($0 \leq s \leq$
 209 1). The term in curly brackets is the sum of Havriliak-Negami (or HN) relaxation functions
 210 with fitting parameters $0 \leq \alpha_j \leq 1$ and $0 \leq \beta_j \leq 1$. For $\beta_j = 1$ (i.e. Cole-Cole or CC function), the
 211 Nyquist plot of such relaxation is a circular arc centered under ε' axis whereas it is a skewed
 212 arc for $\alpha_j = 0$ (Cole-Davidson or CD function). $\Delta\varepsilon_j$ is the dielectric strength and τ_j the mean
 213 relaxation time corresponding to relaxation frequency $\nu_j = (2\pi\tau_j)^{-1}$. The term $A(i\omega)^{s-1}$ with $0 \leq$
 214 $s \leq 1$ can be observed in the low-frequency range for disordered conducting networks at the
 215 macroscopic (sample) scale or to distributions of contact resistances and capacitance between
 216 metallization and the sample. The Nyquist plot of such behavior is a straight line whose angle
 217 $\theta = (1-s)\pi/2$ with the ε' -axis is the smaller as the parameter s is higher: the straight line is
 218 vertical for $s = 0$ and merged with the sample dc-conductivity σ_s . The relaxations can be
 219 evidenced by a decomposition procedure of dielectric spectra due to the additivity of

220 polarizations at the different scales of the sample. Hence, the decomposition procedure of a
221 spectrum is made by successive subtractions of the contributions starting from lower to higher
222 frequencies. The entire Nyquist plots show that the low-frequency parts of the spectrum are
223 well fitted by straight lines (contributions P1) corresponding to the power-law term $A(i\omega)^{s-1}$
224 (Fig. 6-8, Fig. S4-S7 and Table S1). Experimental data show that the parameter s is between 0
225 and 0.06 for all the samples except Li_3N and $\text{Li}_{2.90}\text{Co}_{0.05}\text{N}$ where $s = 0.30$ and 0.4
226 respectively. Less conductive samples (Li_3N and $\text{Li}_{2.90}\text{Co}_{0.05}\text{N}$) have few mobile charge
227 carriers (Li^+), due to a random distribution of lithium vacancies in the conducting planes. The
228 resulting distribution of diffusion lengths increases the tortuosity of the ionic 2D conduction
229 network in Li_3N and $\text{Li}_{2.90}\text{Co}_{0.05}\text{N}$. On the contrary, P1 contributions of the most conductive
230 samples ($\text{Li}_{3-2x}\text{Co}_x\text{N}$ with $0.12 < x < 0.44$) are quasi-merged with that of sample dc-
231 conductivities showing narrow distributions of ionic diffusion lengths. The decomposition
232 procedure of a dielectric spectrum is performed as follows: a) the P2 relaxation is evidenced
233 after subtraction of the P1 contribution; b) the relaxations P3, P4, P5 and P6 are obtained after
234 subtractions of P2, P3, P4 and P5, respectively. Five relaxations are evidenced for the ionic
235 conductors ($\text{Li}_{2.90}\text{Co}_{0.05}\text{N}$ to $\text{Li}_{2.50}\text{Co}_{0.25}\text{N}$) while there are only four for $\alpha\text{-Li}_3\text{N}$ and the
236 electronic conductors ($\text{Li}_{2.36}\text{Co}_{0.32}\text{N}$ to $\text{Li}_{2.12}\text{Co}_{0.44}\text{N}$). Fig. 6-8) show the permittivity Nyquist
237 plots at room temperature of $\text{Li}_{2.64}\text{Co}_{0.18}\text{N}$ (ionic conductor), $\text{Li}_{2.36}\text{Co}_{0.32}\text{N}$ (low electronic
238 conductor) and $\text{Li}_{2.22}\text{Co}_{0.39}\text{N}$ (good electronic conductor), respectively (see Table 2). The
239 Nyquist plots of other samples are described in Supporting Information (Fig. S1-S5). The P2,
240 P3 and P4 dielectric relaxations are due to polarization fluctuations at different scales of the
241 sample. Their corresponding relaxation frequencies are ν_2 , ν_3 and ν_4 , respectively. The first
242 one P2 is attributed to Ag/sample interface giving rise to a space-charge polarization at
243 sample scale. The two others P3 and P4 correspond to the relaxations of the space-charge
244 polarizations of the particles (aggregates of grains) and the grains, respectively. The existence

245 of space-charges are the result of accumulated electrons and lithium ions at particle and grain
 246 surfaces. Relaxation frequencies and dielectric strengths of the three different types of space-
 247 charge polarizations are summarized in Fig. S4-7 and Table S2 of Supporting Information.
 248 Considering all the studied samples, the relaxation frequencies ν_2 , ν_3 and ν_4 are in the
 249 following frequency ranges at room temperature: a) $10^2 < \nu_2 < 3 \times 10^5$ Hz for the silver
 250 paste/sample contribution, b) $6.3 \times 10^4 < \nu_3 < 7 \times 10^7$ Hz for the particle contribution and c)
 251 $1.3 \times 10^7 < \nu_4 < 3.9 \times 10^8$ Hz for the grain contribution (Fig. S4-7 and Table S2). Note, that the
 252 space-charge relaxation following grain polarization (P4) is mainly due to bound charges (Li+
 253 and electrons) at grain surface. Hence, when a grain is submitted to an electric field, charges
 254 are un-trapped from the grain boundary, move through the grain core and tend to be
 255 accumulated on the opposite boundary side. This type of motion needs more activation energy
 256 to perform the transfer, i.e. $E_g > E_i$ or $E_g > E_e$ (Table 2 and S2). The higher frequency
 257 contributions P5 and P6 are thus due to polarization fluctuations within the grain. They are the
 258 consequence of the intrinsic local motions of electrons and lithium ions which are observed in
 259 the samples. The relaxations P5 and P6 are both observed only for the ionic conductors $\text{Li}_{3-2x}\text{Co}_x\text{N}$
 260 with $0.05 \leq x \leq 0.25$. As P5 relaxation is only present for $\alpha\text{-Li}_3\text{N}$, which is a pure
 261 ionic conductor, it allows us to attribute this relaxation to a local Li^+ hopping in the *ab* plane
 262 of the Li_3N structure. The Li^+ hopping is only possible if there is a contiguous lithium
 263 vacancy, i.e. the existence of at least one Li^+ -vacancy pair. According to [24,25], some
 264 vacancies are present in the sample due to small contaminations. Its characteristic frequency
 265 $\nu_i = 6 \times 10^8$ Hz at room temperature (Table 2) follows the Arrhenius law with an activation
 266 energy of about 0.19 eV and a prefactor $\nu_{0i} = 9 \times 10^{11}$ Hz. For samples $\text{Li}_{2.90}\text{Co}_{0.05}\text{N}$,
 267 $\text{Li}_{2.76}\text{Co}_{0.12}\text{N}$ and $\text{Li}_{2.64}\text{Co}_{0.18}\text{N}$, P5 relaxations have characteristic frequencies of the same
 268 order of magnitude than that of Li_3N with similar activation energies E_i between 0.19 and
 269 0.20 eV (Fig.9a and Table 2) and prefactors ν_{0i} between 9.0×10^{11} and 1.1×10^{12} Hz (Fig. 9a

270 and Table 2). For samples $\text{Li}_{2.90}\text{Co}_{0.05}\text{N}$ to $\text{Li}_{2.64}\text{Co}_{0.18}\text{N}$ (electronic insulators), the P6
 271 relaxation is due to the fast motion of the electrons on isolated cobalt clusters with
 272 characteristic frequencies ν_e ranking between 2.7×10^9 and 3.7×10^9 Hz at room temperature
 273 (Fig. 9b and Table 2). These frequencies ν_e are also thermally activated, with activation
 274 energies E_e of about 0.18 - 0.20 eV (Fig. 9a-c) and prefactors ν_{0e} in the range 3×10^{12} - 4×10^{12}
 275 Hz (Table 2). The ionic conductor $\text{Li}_{2.50}\text{Co}_{0.25}\text{N}$ is a special case, because the relaxation
 276 frequency of P5 attributed to Li^+ motion ($\nu_i = 10^{10}$ Hz with $E_i = 0.19$ eV), is higher than P6
 277 relaxation frequencies, attributed to electrons⁻ in Co clusters ($\nu_e = 1.2 \times 10^9$ Hz with $E_e = 0.25$
 278 eV) (Fig. 9b) and Table 2). As the activation energy of the local motion must be less than or
 279 equal to that of the grain conductivity (i.e. $E_g = 0.21$ eV), the attributions of P5 and P6 are
 280 thus justified for $\text{Li}_{2.50}\text{Co}_{0.25}\text{N}$. Indeed, based on the conductivity analysis, which indicates the
 281 ionic nature of $\text{Li}_{2.50}\text{Co}_{0.25}\text{N}$ conduction, and the lower activation energy of P5 relaxation
 282 regards the grain activation energy E_g , the Li^+ ionic motion is ascribed to the highest
 283 relaxation frequency (with $\nu_i = 10^{10}$ Hz). For electronic conductors ($\text{Li}_{2.36}\text{Co}_{0.32}\text{N}$,
 284 $\text{Li}_{2.22}\text{Co}_{0.39}\text{N}$ and $\text{Li}_{2.12}\text{Co}_{0.44}\text{N}$), only local electronic motions corresponding to P6 are
 285 observed (Fig. 7, 8) and S7). Frequencies ν_e are thermally activated with activation energies
 286 E_e of about 0.18-0.20 eV (Fig. 9c) and prefactors ν_{0e} in the range 6×10^{11} - 4.6×10^{12} Hz (Table
 287 2). The P6 relaxation is fitted by Debye functions for $\text{Li}_{2.22}\text{Co}_{0.39}\text{N}$ and $\text{Li}_{2.12}\text{Co}_{0.44}\text{N}$, and by a
 288 CD-function for $\text{Li}_{2.36}\text{Co}_{0.32}\text{N}$ (Fig. 7) and Table 2). Relaxation frequencies (ν_i and ν_e) and
 289 dielectric strengths ($\Delta\epsilon_i$ and $\Delta\epsilon_e$) for ion and electron motions are respectively minimum and
 290 maximum as a function of x (Fig. 9 d and e). The origin of these behaviors will be fully
 291 developed in the next section.

292 3.3. Origin of ionic and electronic conductivities: evidence of percolations in $\text{Li}_{3-2x}\text{Co}_x\text{N}$

293 Like for the grain conductivities, the activation energies of the relaxation frequencies
 294 ν_i and ν_e are similar because ions and electrons undergo the same attractive electrostatic
 295 interactions to move through the crystal lattice (Table 2). The following expression [34,35],

$$296 \quad \frac{\sigma_g}{2\pi p \varepsilon_0 \Delta \varepsilon_k} = \nu_k \quad (8)$$

297 shows that the experimental findings described in Fig. 10 are well fitted with the correlation
 298 factor $p \approx 1$. Here σ_g is the grain conductivity, $\Delta \varepsilon_k$ the dielectric relaxation strength and ν_k the
 299 relaxation frequency where the subscript k corresponds to i for ionic conductors and to e for
 300 electronic conductors (see Table 2). Consequently, inner grain conduction and local
 301 polarization have the same origin in $\text{Li}_{3-2x}\text{Co}_x\text{N}$, whatever the type of charge carrier (electron
 302 or ion). Fig. 4 shows significant rises of ionic and electronic conductivities for x above 0.11
 303 and 0.30, respectively. Dielectric strengths ($\Delta \varepsilon_5$ and $\Delta \varepsilon_6$) and relaxation frequencies (ν_5 and
 304 ν_6) exhibit critical behaviors near of the same x contents. These behaviors can be likened to
 305 percolation transitions according to the predictive percolation models on conductivity,
 306 permittivity and relaxation frequency [36,37,38,39,40,41] (see Supporting Information S4).
 307 Furthermore, the CD function, which fits the relaxation P6 in $\text{Li}_{2.36}\text{Co}_{0.32}\text{N}$ (i.e. $x = 0.32$) (Fig.
 308 7) is justified by previous computational and theoretical models for systems slightly above of
 309 the percolation threshold [42,43].

310 Fig. 11a and b show the distribution of cobalt ions in the crystal lattice perpendicular
 311 to c -axis for $x = 0.18$ and $x = 0.44$, respectively. As the Co^{2+} cations substitute Li^+ cations in
 312 the $1b$ sites (interlayer space), the electronic transfer is expected to occur only in the two-
 313 dimensional triangular lattice formed in the ab plane for $x > x_{ce} \approx 0.30$ (Fig. 11b). Then, a 2D
 314 continuous network of cobalt ions appears which facilitates electronic transfers between Co
 315 ions. This finding suggests the presence of a small amount of Co^+ ions. For $x > 0.30$ and
 316 outside the critical region (i.e. $x = 0.39$ and 0.44), the experimental data can be fitted by a

317 straight line which is described by the expression of the effective medium approximation for
 318 bond percolation (EMA theory [40,41]):

$$319 \quad \sigma_{ge} = \sigma_m \left[\frac{z}{z-2} x - \frac{2}{z-2} \right] \quad (2)$$

320 where σ_{ge} is the grain electronic conductivity, a fitting parameter $\sigma_m \approx 18 \text{ S m}^{-1}$ (i.e.
 321 maximum electronic conductivity) and $z = 6.06$, the cobalt coordination number. This result is
 322 in good agreement with observed 2D bond percolation in our triangular lattice ($z = 6$ and $x_{ce} \approx$
 323 0.33).

324 On the contrary, Li^+ diffusion can have a three-dimensional character, especially for
 325 some x values as discussed below. Indeed, since the percolation thresholds on 2D networks
 326 are higher than those of 3D networks, the second threshold at $x_{ci} \approx 0.10 - 0.12$ corresponds to
 327 a 3D percolation of the ionic conductivity σ_{gi} of $\text{Li}_{3-2x}\text{Co}_x\text{N}$ grains. The rise of the ionic
 328 conductivity is here due to the increase of the number of lithium vacancies and thus, to Li^+
 329 motions. For $x < 0.11$, $\text{Li}^+(2c)$ ions only diffuse in ab planes thanks to the presence of a
 330 limited number of lithium vacancies. The lithium diffusion mechanism is then expected to be
 331 similar to the diffusion process encountered in Li_3N , where the Li^+ conductivity was
 332 explained by the presence of 1 or 2% of lithium vacancies due to structural defects or
 333 hydrogen contamination [44]. Since for $x < 0.11$, the number of lithium vacancies induced by
 334 the limited amount of Co^{2+} present in the structure, similar diffusion paths are expected with
 335 conductivity of same order of magnitude. For $0.11 < x < 0.25$, the number of lithium
 336 vacancies is such that $\text{Li}^+(2c)$ ions, i.e. Li ions in the $\text{Li}_{2-x}\text{N}^-$ planes, might diffuse in both
 337 parallel directions to ab planes (in the $\text{Li}_{2-x}\text{N}^-$ planes) and also along the c -axis. However, for
 338 x between 0.25 and 0.32, the ionic conductivity drops to ~ 0 , where the percolation of the
 339 electronic conductivity takes place (Fig. 4). It does not indicate the full disappearance of the
 340 ionic conductivity, only that the ionic conductivity becomes negligible regards to the true in-
 341 plane electronic contribution. Long-range motions of $\text{Li}^+(2c)$, might be blocked along the c -

342 axis by the percolated network of the cobalt ions, which leads to strong electrostatic
 343 repulsions. The ionic conductivity should come back to a 2D regime within the layer (2c site),
 344 with more space for Li^+ transport via vacancies (increasing content with x). However, $\text{Li}(2c)$
 345 has an increasing number of nearest Co^{2+} neighbor on 1b sites in surrounding layers (upper
 346 and lower, Fig. 1d and Fig. 11b). As the repulsive coulombic interactions between $\text{Li}^+(2c)$ and
 347 $\text{Co}^{2+}(1b)$ for $x > 0.30$ are higher than those between $\text{Li}^+(2c)$ and $\text{Co}^{2+}(1b)$ for $x < 0.11$, the Li^+
 348 (2c) transport should be slowed down. This results in a higher activation energy of the ionic
 349 conductivity, which therefore, becomes smaller and thus negligible compared to the electronic
 350 conductivity. Local polarizations attributed to ion local motion, are not detectable because
 351 dielectric strengths $\Delta\epsilon$ corresponding to their dielectric responses become small according to
 352 the percolation theory (Supporting Information S4). Moreover, the plot of $\sigma_{\text{gi}} = f(x)$ does not
 353 allow a full description of the 3D ionic percolation. The ionic conductivity σ_{gi} usually
 354 depends on the mobile ions concentration whose mobility increases with the vacancies
 355 concentration. It is then more suitable to represent the conductivity σ_{gi} as a function of $y = (2-$
 356 $x)x$, where $(2-x)$ is the number of mobile $\text{Li}^+(2c)$ and x the number of Li^+ vacancies in the 2c
 357 site of a single unit cell. The dependence of σ_{gi} with y is plotted in Figure 11c. A percolation
 358 threshold at $y_{\text{ci}} = (2-x_{\text{ci}})x_{\text{ci}} \approx 0.23$ is suggested. Then, y_{ci} value is consistent with a 3D
 359 percolation scheme with an ionic coordination number included between 8 and 12. In our
 360 case, when considering the two layers surrounding the layer of the $\text{Li}^+(2c)$ ion which will
 361 diffuse, 11 possible neighboring sites are numbered: 3 in the same ab plane, as for the 2D
 362 diffusion scheme observed for $x < 0.11$, and 4 sites per surrounding layer (Fig. 11d). Since
 363 lithium diffusion is only possible if at least one of the neighboring sites is occupied by a
 364 lithium vacancy, only a smooth increase of the conductivity at the percolation threshold y_{ci} is
 365 evidenced according to a smooth transition from low to high conductivity behavior. In this
 366 case, the ionic conductivity $\sigma_{\text{gi}}(y_{\text{ci}})$ at the percolation threshold is thus given by:

$$\sigma_{gi}(y_{ci}) = \sigma_L \left(\frac{\sigma_L}{\sigma_H} \right)^q \quad (3)$$

where σ_L is the ionic conductivity of Li_3N (*low electrical conductor*), σ_H the maximum ionic conductivity (*high electrical conductor*) that would be obtained at $y = 1$ and $q \approx 0.72$ for a 3D conductor [45]. Since $\sigma(y_{ci}) \approx 0.5 \text{ S m}^{-1}$ and $\sigma_L = 0.1 \text{ S m}^{-1}$ at room temperature, the relation (3) gives $\sigma_H \approx 31 \text{ S.m}^{-1}$. When $y > y_{ci}$, the conductivity increases with y as:

$$\sigma_{gi}(y) = \sigma_H \left(\frac{y - y_{ci}}{1 - y_{ci}} \right)^t \quad (4)$$

where t is a critical parameter. Considering the conductivity values for $y > 0.23$ (or $x > 0.12$) and $\sigma_H = 31 \text{ S.m}^{-1}$, Eq. 4 gives $t = 1.6$ for $y = 0.33$ (or $x = 0.18$) and $t = 1.8$ for $y = 0.42$ (or $x = 0.24$). This range of values of t is a suitable result for a 3D conductor given the margin of error.

Evolutions of grain conductivity and of dielectric relaxation parameters (dielectric strength and relaxation frequency) with Co content x confirm the two percolation transitions of ionic and electronic conductivities. The grain conductivity has a large discontinuity immediately below the electronic percolation threshold where any local- and long-range ionic movement become progressively negligible without electronic transfer. This discontinuity would be due to a narrow transition from ionic to electronic conduction when x increases.

4. Conclusion

For the first time, broadband dielectric spectroscopy from 60 to 10^{10} Hz has been applied to study both ionic and electronic transport properties of $\text{Li}_{3-2x}\text{Co}_x\text{N}$ solid-solution compounds. It has been possible using BDS to discriminate all the contributions of the conductivity. These successive relaxations appear with increasing frequency according to the following order: (a) sample/silver paint interface; (b) particles (aggregates of grains); (c) grains (crystallites); (d) local ionic and electronic motions within the grains. Complex plane plots of resistivity, conductivity and permittivity are thus used to determine grain (or intrinsic) conductivity and

391 to evidence dielectric relaxations at different scales of the samples from low to microwave
392 frequency range. Surprisingly, even if the structural parameters evolve linearly with the cobalt
393 content, three different conduction regimes are evidenced, separated by two percolation
394 transitions. The first percolation threshold, at $x \approx 0.11$, is associated to a transition from 2D to
395 3D ionic conduction regimes. This ionic conductivity increases significantly after the
396 percolation threshold of more than an order of magnitude to reach $\sigma_{gi} \approx 2.6 \text{ S m}^{-1}$ at room
397 temperature. Then, the second threshold at $x \approx 0.30$, results from the percolation of the Co
398 ions leading to continuous 2D electronic conductive network. The electronic conductivity
399 reaches an effective value close to $\sigma_{ge} \approx 3 \text{ S m}^{-1}$ for the highest cobalt content at room
400 temperature. In reality, the true 2D electronic conductivity is higher than its effective value
401 σ_{ge} , which is measured in a 3D isotropic sample. Surprisingly, the both movements have
402 similar activation energies ($0.19 \text{ eV} < E_i < 0.21 \text{ eV}$ and $0.19 \text{ eV} < E_e < 0.23 \text{ eV}$). This finding
403 might be related to the existence of the same Coulomb interactions felt by the electrons and
404 the lithium cations. Moreover, ionic conduction becomes negligible beyond the electronic
405 percolation threshold ($x \approx 0.30$). The transport of lithium ions could be slowed by the
406 presence of a growing number of cobalt ions which creates strong electrostatic repulsions.
407 Experimental values of dielectric strengths and relaxation frequencies associated to the
408 intrinsic local ionic and electronic motions are well described by the percolation theory. The
409 present finding demonstrates the relevance of BDS analysis to discriminate the intrinsic
410 conductive properties of powdered samples.

411

412 **Table 1.** Composition, cell parameters and volume of the $\text{Li}_{3-2x}\text{Co}_x\text{N}$ solid-solution samples. The
 413 composition were determined through Rietveld refinement of powder XRD data with the lithium
 414 content fixed to 3-2x

Composition	a (Å)	c (Å)	Volume (Å ³)
Li_3N	3.667(7)	3.876(8)	45.1(2)
$\text{Li}_{2.90}\text{Co}_{0.05(2)}\text{N}$	3.669(7)	3.861(8)	45.0(2)
$\text{Li}_{2.76}\text{Co}_{0.12(2)}\text{N}$	3.678(7)	3.826(8)	44.8(2)
$\text{Li}_{2.64}\text{Co}_{0.18(2)}\text{N}$	3.687(7)	3.807(7)	44.8(2)
$\text{Li}_{2.50}\text{Co}_{0.25(2)}\text{N}$	3.692(7)	3.767(7)	44.5(2)
$\text{Li}_{2.36}\text{Co}_{0.32(2)}\text{N}$	3.712(7)	3.724(7)	44.4(2)
$\text{Li}_{2.22}\text{Co}_{0.39(2)}\text{N}$	3.716(7)	3.704(7)	44.2(2)
$\text{Li}_{2.12}\text{Co}_{0.44(2)}\text{N}$	3.730(7)	3.652(7)	44.0(2)

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420 **Table 2.** Intrinsic grain contributions: grain dc-conductivity and dielectric relaxations due to
 421 local motions of electrons and lithium cations.

$\text{Li}_{3-2x}\text{Co}_x\text{N}$	dc-conductivity	Li ⁺ motions (P5)		Electron motions (P6)		High- frequency Permittivity
		σ_g (S.m ⁻¹) E_g (eV)	ν_i (Hz) E_i (eV) α_i	ν_{0i} (Hz) $\Delta\epsilon_i$ β_i	ν_e (Hz) E_e (eV) α_e	
Li₃N						
x = 0.00*	0.10 0.19	6.0×10^8 0.19 0.13	9.0×10^{11} 3 0			9.3
Li_{2.90}Co_{0.05}N						
x = 0.05*	0.20 0.19	6.0×10^8 0.19 0	9.0×10^{11} 6.5 0	3.0×10^9 0.18 0.26	3.0×10^{12} 1.4 0	9.3
Li_{2.76}Co_{0.12}N						
x = 0.12*	0.50 0.21	2.0×10^8 0.21 0.15	9.8×10^{11} 28 0	2.5×10^9 0.18 0.10	2.7×10^{12} 3.7 0	11.1
Li_{2.64}Co_{0.18}N						
x = 0.18*	1.30 0.20	5.0×10^8 0.20 0.03	1.1×10^{12} 26 0	3.7×10^9 0.18 0.08	3.7×10^{12} 6.0 0	12.7
Li_{2.50}Co_{0.25}N						
x = 0.25*	2.60 0.21	1.0×10^{10} 0.19 0.19	1.4×10^{13} 4.6 0	1.2×10^9 0.25 0.08	1.5×10^{13} 18 0	14.5
Li_{2.36}Co_{0.32}N						
x = 0.32**	0.56 0.23			2.3×10^8 0.20 0	6.0×10^{11} 36 0.40	11
Li_{2.22}Co_{0.39}N						
x = 0.39**	1.50 0.20			1.1×10^9 0.19 0.11	1.5×10^{12} 26 0	16.5
Li_{2.12}Co_{0.44}N						
x = 0.44**	3.00 0.19			4.5×10^9 0.18 0	4.6×10^{12} 6.0 0	15

422

* Ionic conductors; ** Electronic conductors.

423

424

425 **Figure Captions**

426 **Figure 1.** (a) X-Ray diffraction patterns of the $\text{Li}_{3-2x}\text{Co}_x\text{N}$ samples; (b) Hexagonal structure
 427 ($\text{P6}_m\text{mm}$) of $\text{Li}_{3-2x}\text{Co}_x\text{N}$ phases. Co^{+2} ions substitute Li^+ ions in the 1b site (in green), leading
 428 to the creation of an equivalent amount of vacancies \square in the 2c Li^+ site (in red). N^{3-} ions
 429 filled the 1a site.

430 **Figure 2.** Real parts of : a) conductivity σ' and b) permittivity ϵ' vs. frequency of $\text{Li}_{3-2x}\text{Co}_x\text{N}$
 431 for different values of x at 300 K: x = 0, 0.05, 0.12, 0.25, 0.32, 0.39 and 0.44.

432 **Figure 3.** Nyquist plots of the complex resistivity (ρ'' vs. ρ') at 300 K for the samples: a)
 433 $\text{Li}_{2.76}\text{Co}_{0.12}\text{N}$ (LCN2) and b) $\text{Li}_{2.22}\text{Co}_{0.39}\text{N}$ (LCN6). At the top of a) and b): entire plots from
 434 60 to 10^{10} Hz and evidence of low-frequency contributions R1; at the bottom of a) and b):
 435 plots obtained after subtracting R1 and evidence of contributions R2. σ_g corresponds to grain
 436 dc-conductivity.

437 **Figure 4.** (a) Grain conductivity vs. molar cobalt content x: ionic (●) and electronic (●)
 438 conductivities.

439 **Figure 5.** Grain conductivity σ_g vs. inverse temperature $1/T$ for $\text{Li}_{3-2x}\text{Co}_x\text{N}$: a) ionic
 440 conductors (x = 0, 0.05, 0.12 and 0.25) and b) electronic conductors (x = 0.32, 0.39 and 0.44).

441 **Figure 6.** Nyquist plots of the imaginary part $\epsilon''(\omega)$ vs. the real part $\epsilon'(\omega)$ of the complex
 442 permittivity at 300 K for the sample $\text{Li}_{2.76}\text{Co}_{0.12}\text{N}$ (LCN2): a) entire plot from 40 to 10^{10} Hz:
 443 only the low frequency contribution P1 is visible; b) plot obtained upon subtracting the
 444 domain P1: evidence of the relaxation domains P2 and P3; c) plot obtained upon subtracting
 445 domains P2 and P3: evidence of the relaxation domain P4; d) plot obtained upon subtracting
 446 the domain P4: evidence of the relaxation domain P5; e) plot obtained upon subtracting the
 447 domain P5: evidence of the relaxation domain P6.

448 **Figure 7.** Nyquist plots of the imaginary part $\varepsilon''(\omega)$ vs. the real part $\varepsilon'(\omega)$ of the complex
 449 permittivity at 300 K for the sample $\text{Li}_{2.36}\text{Co}_{0.32}\text{N}$ (LCN5): a) entire plot from 40 to 10^{10} Hz:
 450 only the low frequency contribution P1 is visible; b) plot obtained upon subtracting the
 451 domain P1: evidence of the relaxation domains P2 and P3; c) plot obtained upon subtracting
 452 domains P2 and P3: evidence of the relaxation domain P4; d) plot obtained upon subtracting
 453 the domain P4: evidence of the relaxation domain P6.

454 **Figure 8.** Nyquist plots of the imaginary part $\varepsilon''(\omega)$ vs. the real part $\varepsilon'(\omega)$ of the complex
 455 permittivity at 300 K for the sample $\text{Li}_{2.22}\text{Co}_{0.39}\text{N}$ (LCN6): a) entire plot from 40 to 10^{10} Hz:
 456 only the low frequency contribution P1 is visible; b) plot obtained upon subtracting the
 457 domain P1: evidence of the relaxation domains P2 and P3; c) plot obtained upon subtracting
 458 domains P2 and P3: evidence of the relaxation domain P4; d) plot obtained upon subtracting
 459 the domain P4: evidence of the relaxation domain P6.

460 **Figure 9.** Relaxation frequencies as function of inverse temperature for: (a) $x = 0.12$ (Li^+
 461 motions = ■ and electron motions = ■), (b) $x = 0.25$ (Li^+ motions = ■ and electron motions =
 462 ■), (c) $x = 0.44$ (■), 0.39 (■) and 0.32 (■) (electron motions). (d) Relaxation frequencies of
 463 lithium ions (■) and electrons (■) motions as function of x at 293 K. (e) Dielectric strength $\Delta\varepsilon$
 464 as function of x for relaxations due to ion (■) and electron motions (■) at 293 K

465 **Figure 10.** a) Comparison of the dielectric relaxation frequency ν_k (at 300 K) with $\sigma_g/2\pi\varepsilon_0\Delta\varepsilon_k$
 466 which is the ratio the grain conductivity σ_g to the relaxation dielectric strength
 467 $\Delta\varepsilon_k$ ($\alpha\tau$ 300 K) divided by the factor $2\pi\varepsilon_0 = 5.56 \times 10^{-11}$ F.m⁻¹ (*subscripts $k = i$ and e*
 468 *correspond to ionic and electronic motions, respectively*).

469 **Figure 11.** (a) Distribution of cobalt ions in crystal lattice perpendicular to c -axis for: (a) $x =$
 470 0.18 and (b) $x = 0.44$; (c) Grain conductivity vs. molar cobalt content $y = (2-x)x$ ionic where
 471 $(2-x)$ is the concentration of mobile Li^+ cations and x the concentration of Li^+ vacancies on

472 2c sites. (d) Schematic 3D percolation of Li^+ conduction where each $\text{Li}^+(2)$ ion has 11
473 neighboring possible sites considering the transfers parallel to the c axis and to the (2c) plane.

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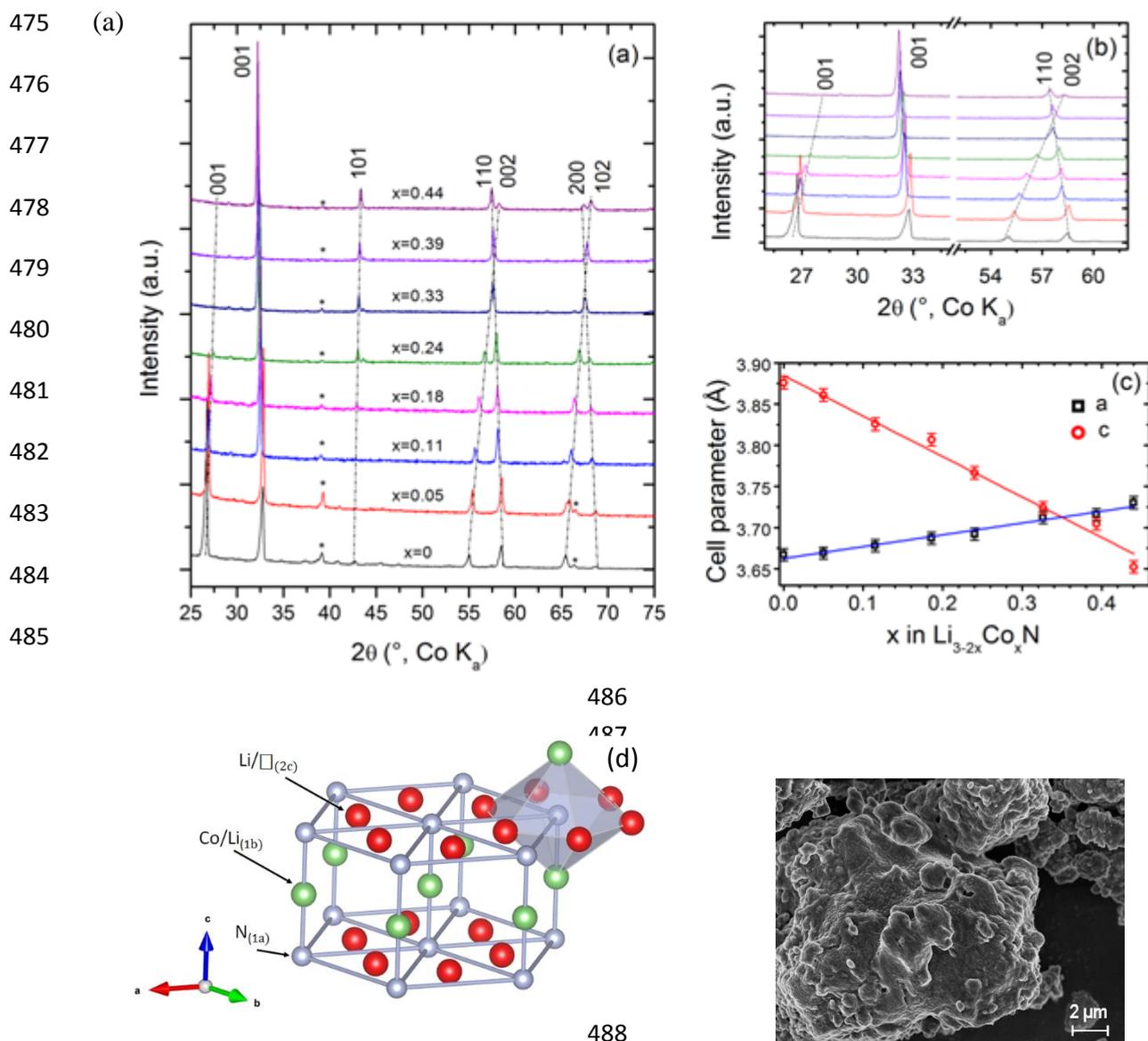
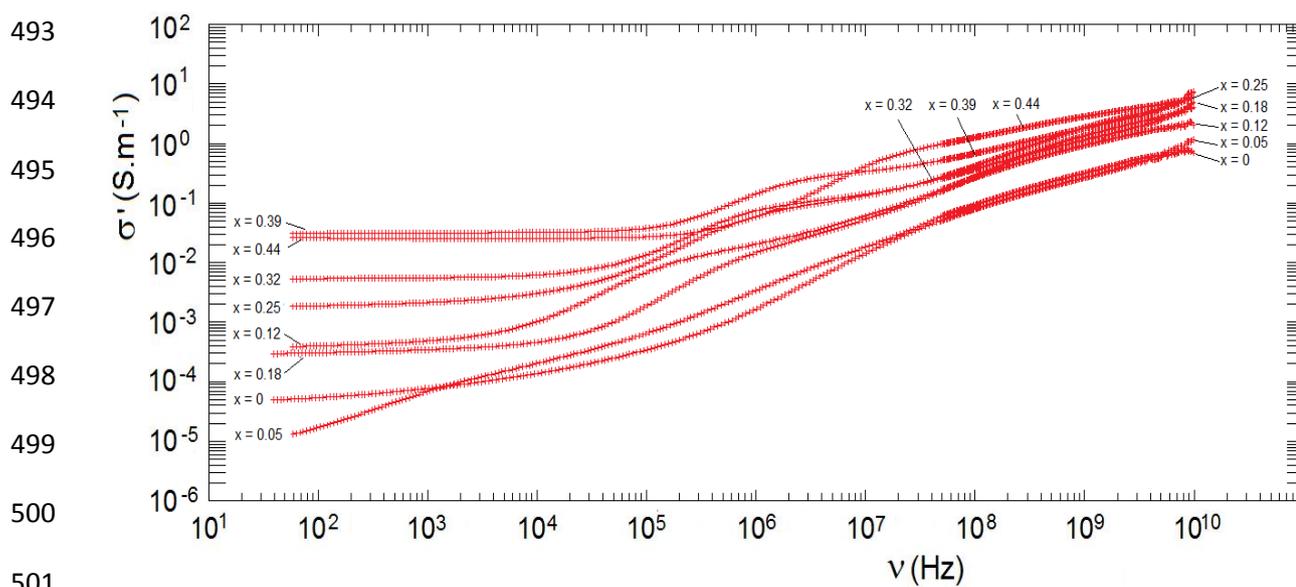
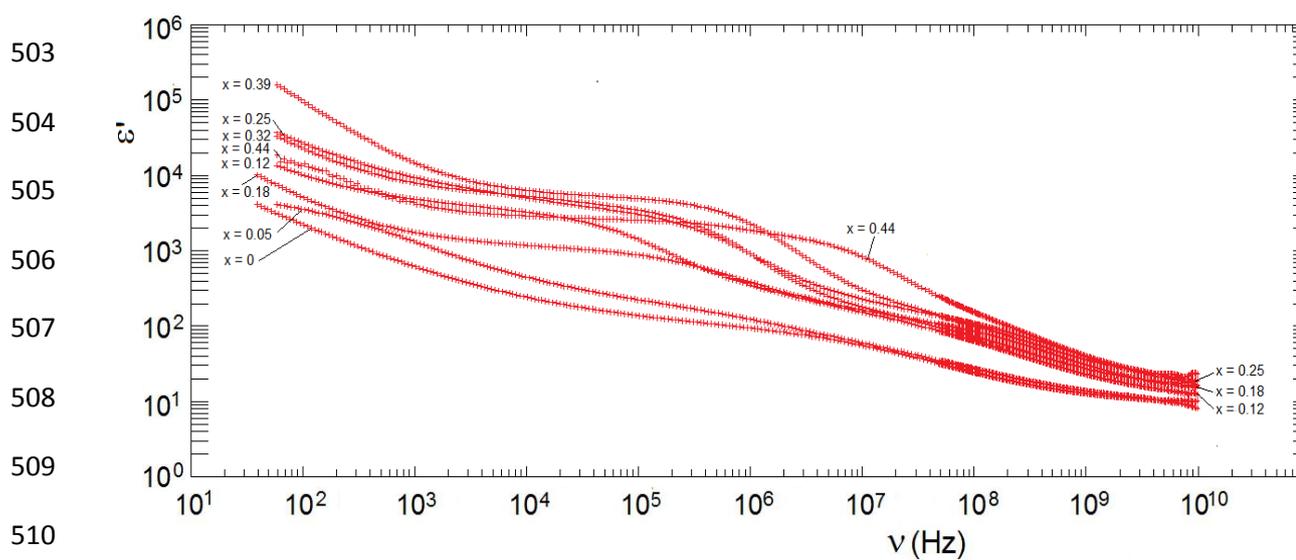


Figure 1.

492 (a)



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514 **Figure 2**

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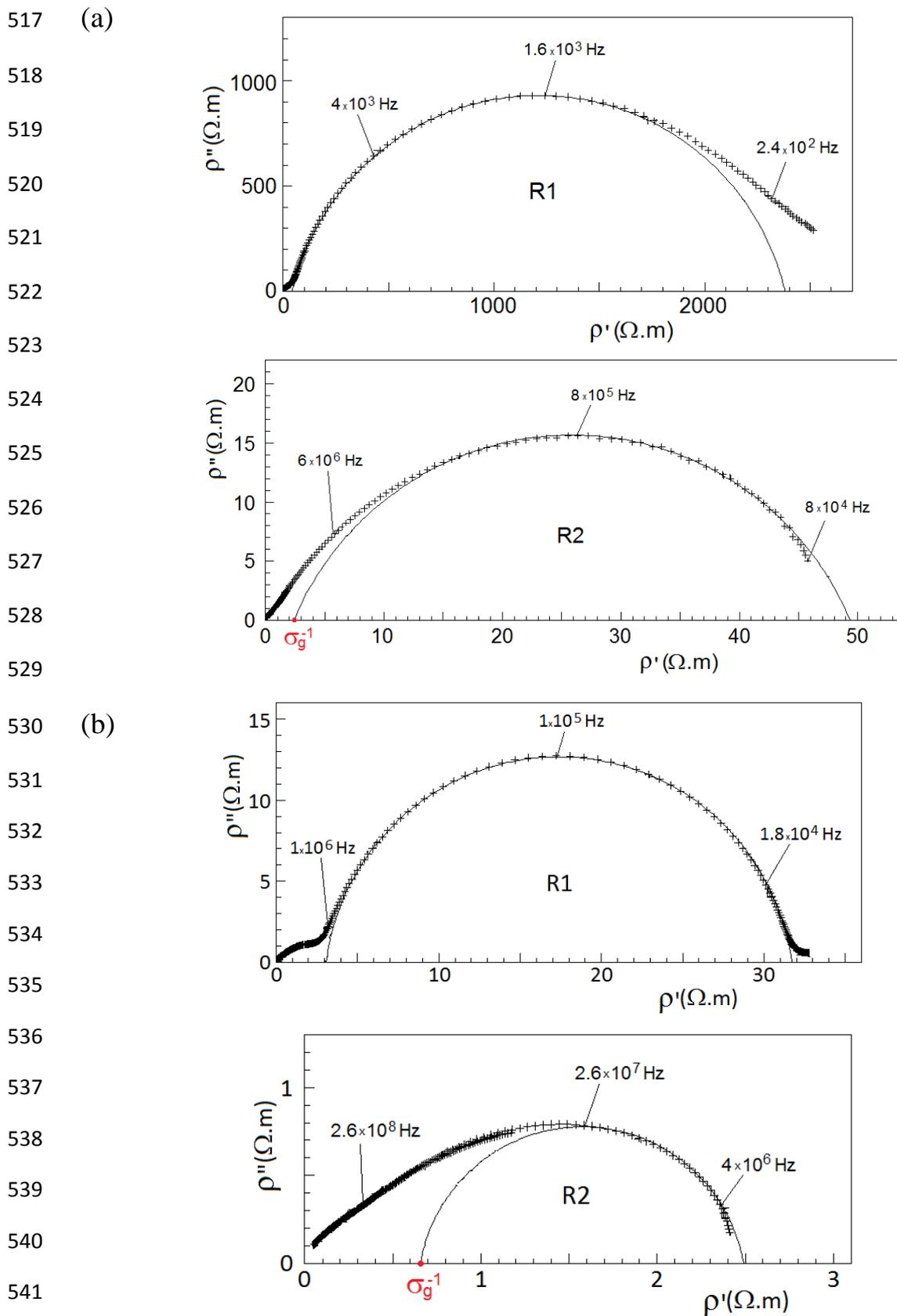


Figure 3.

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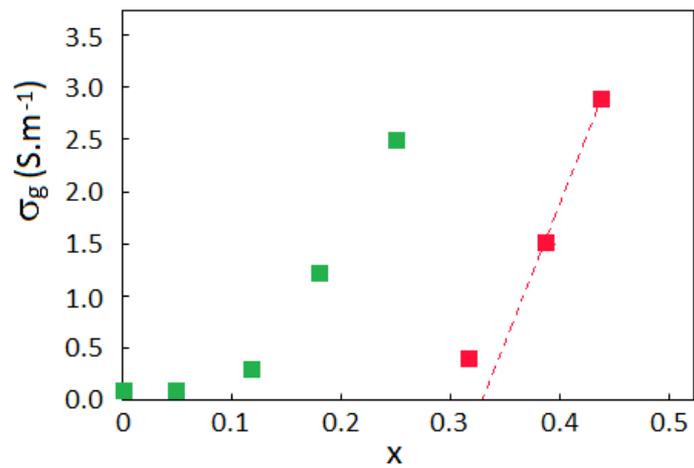
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566 **Figure 4.**

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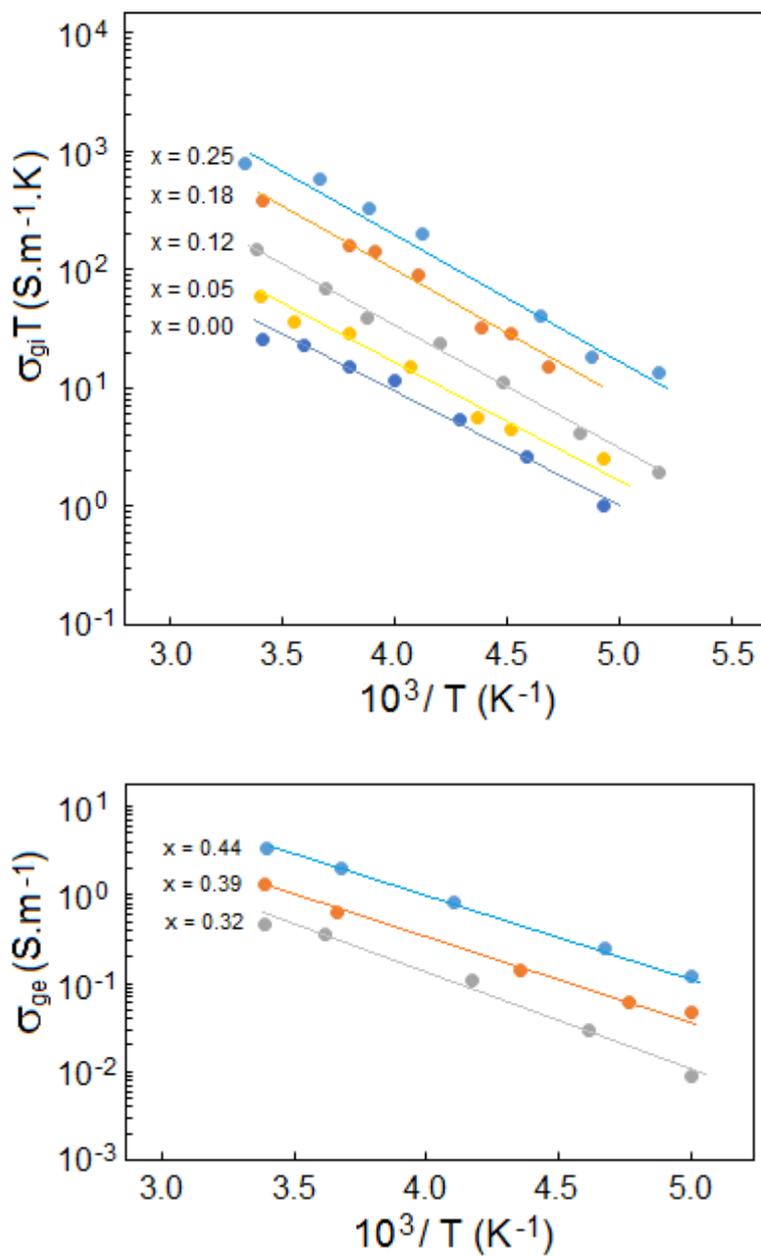
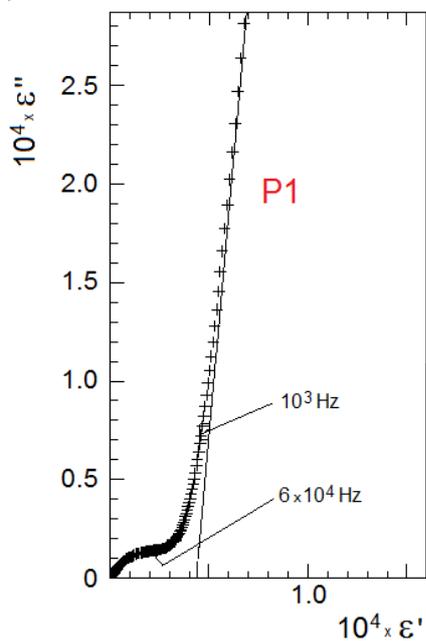


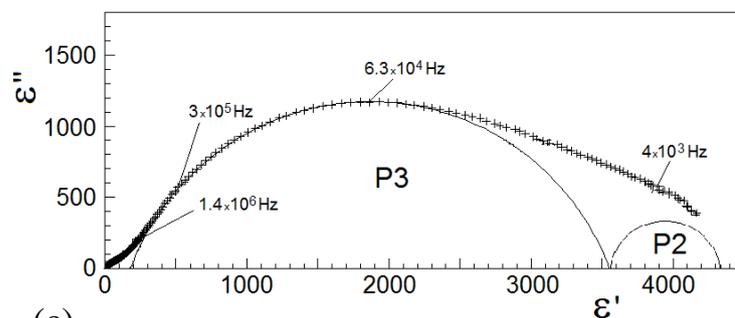
Figure 5.

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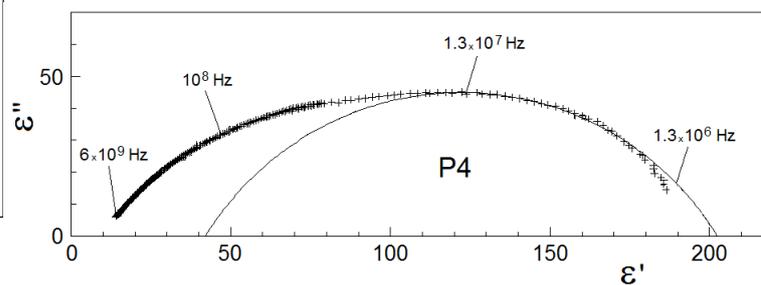
591 (a)



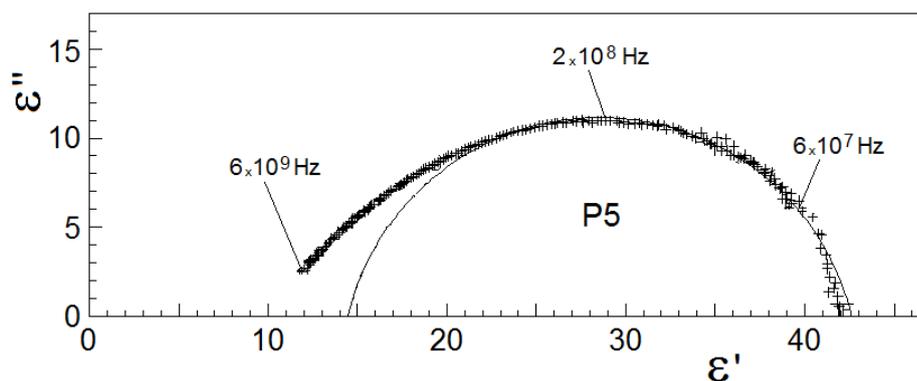
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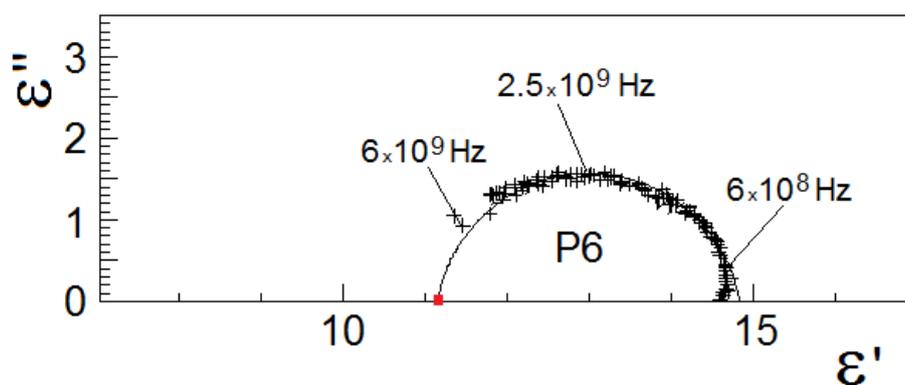
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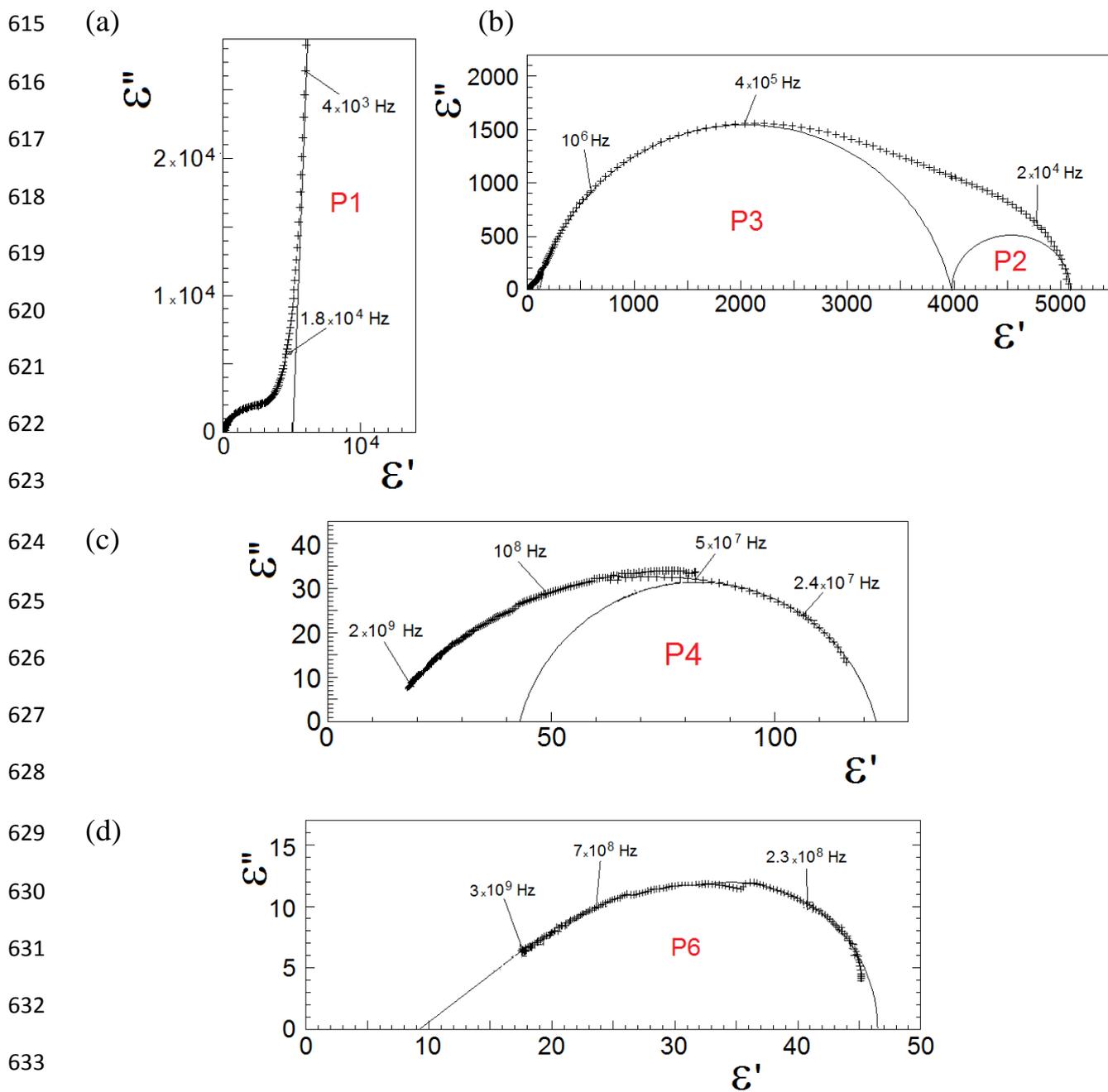
(d)



(e)

613 **Figure 6.**

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634 **Figure 7**

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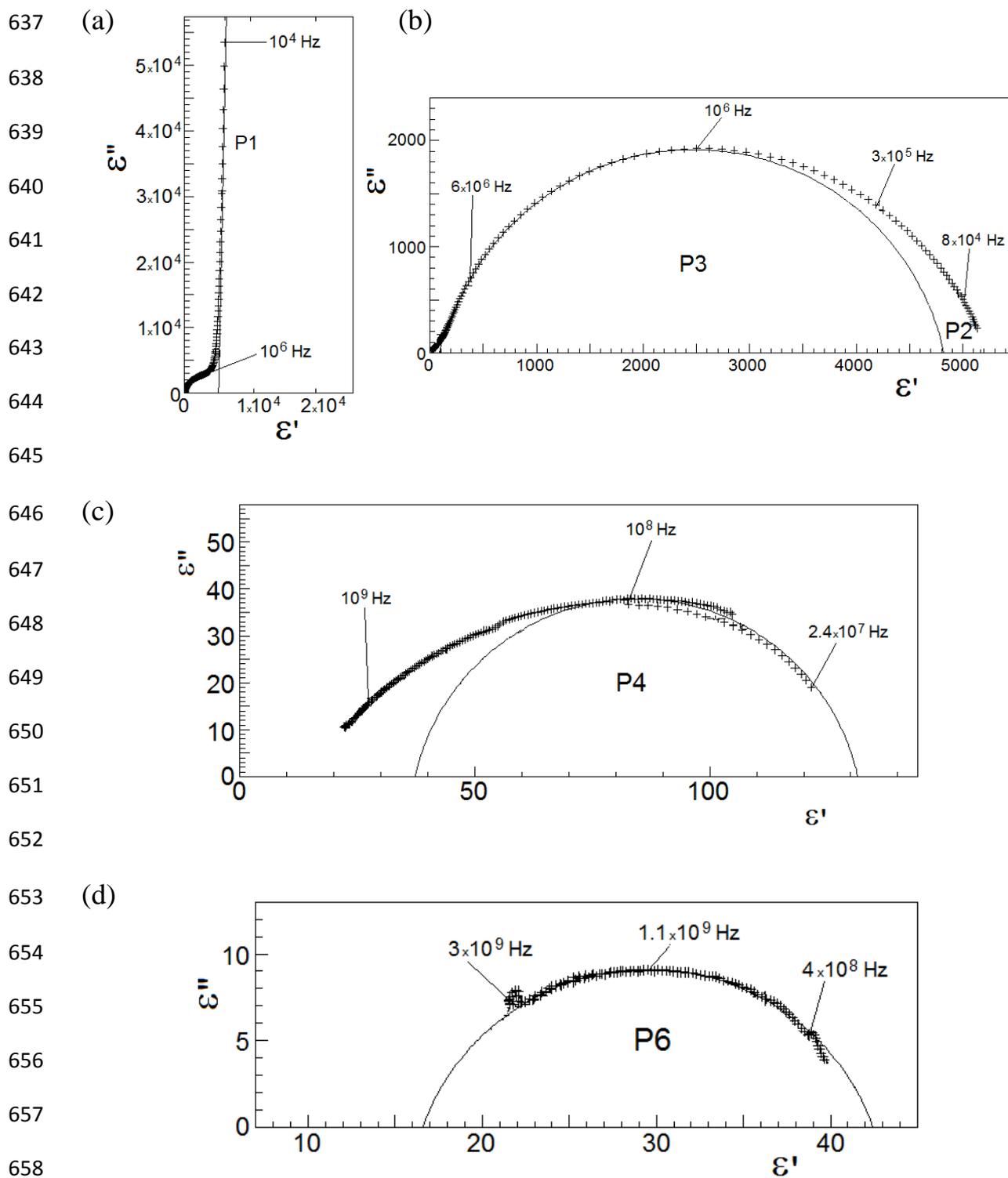
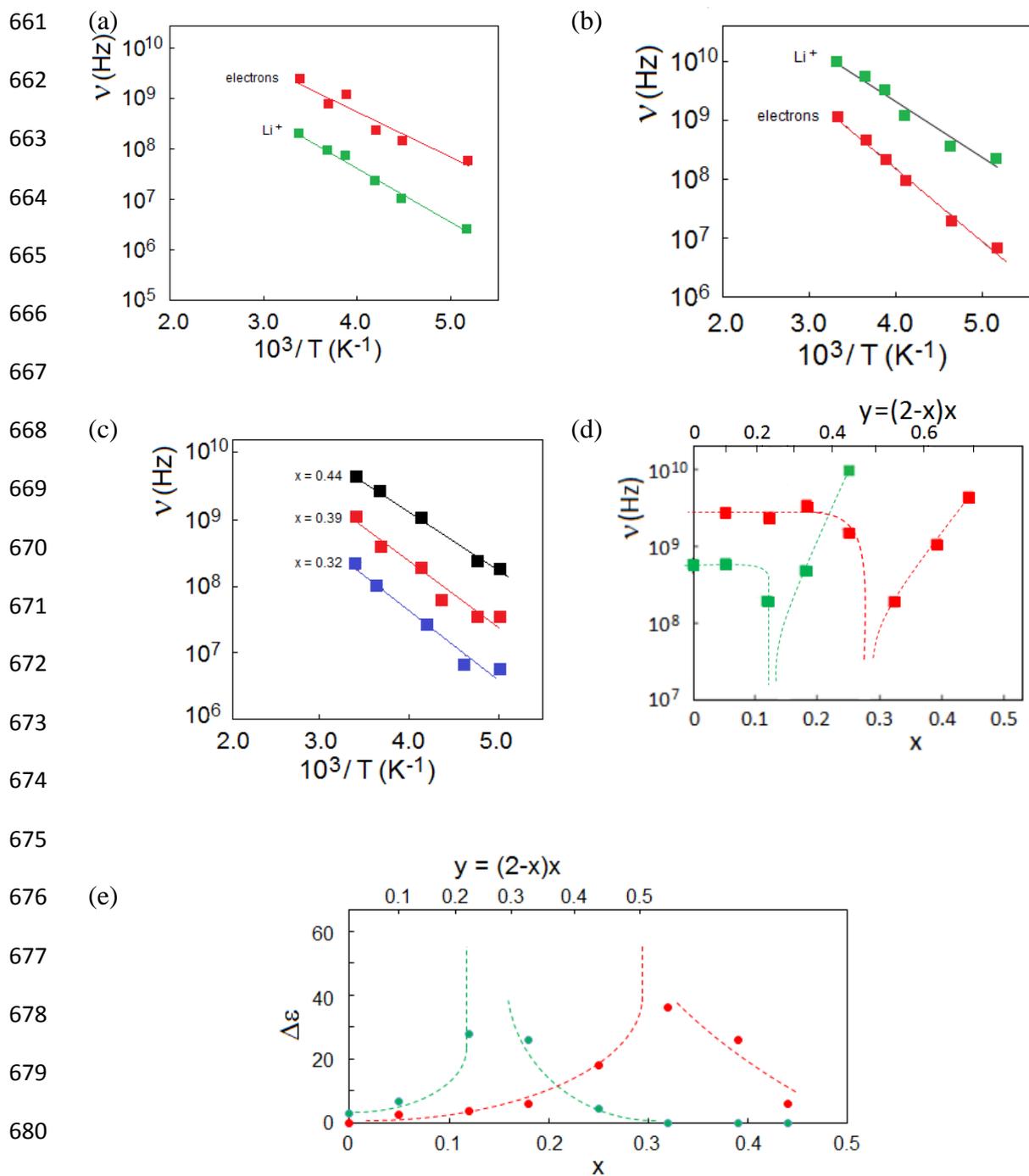


Figure 8.

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684 **Figure 9**

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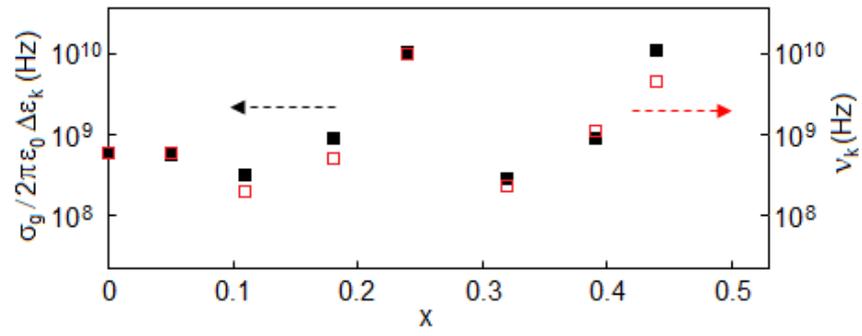
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699 **Figure 10.**

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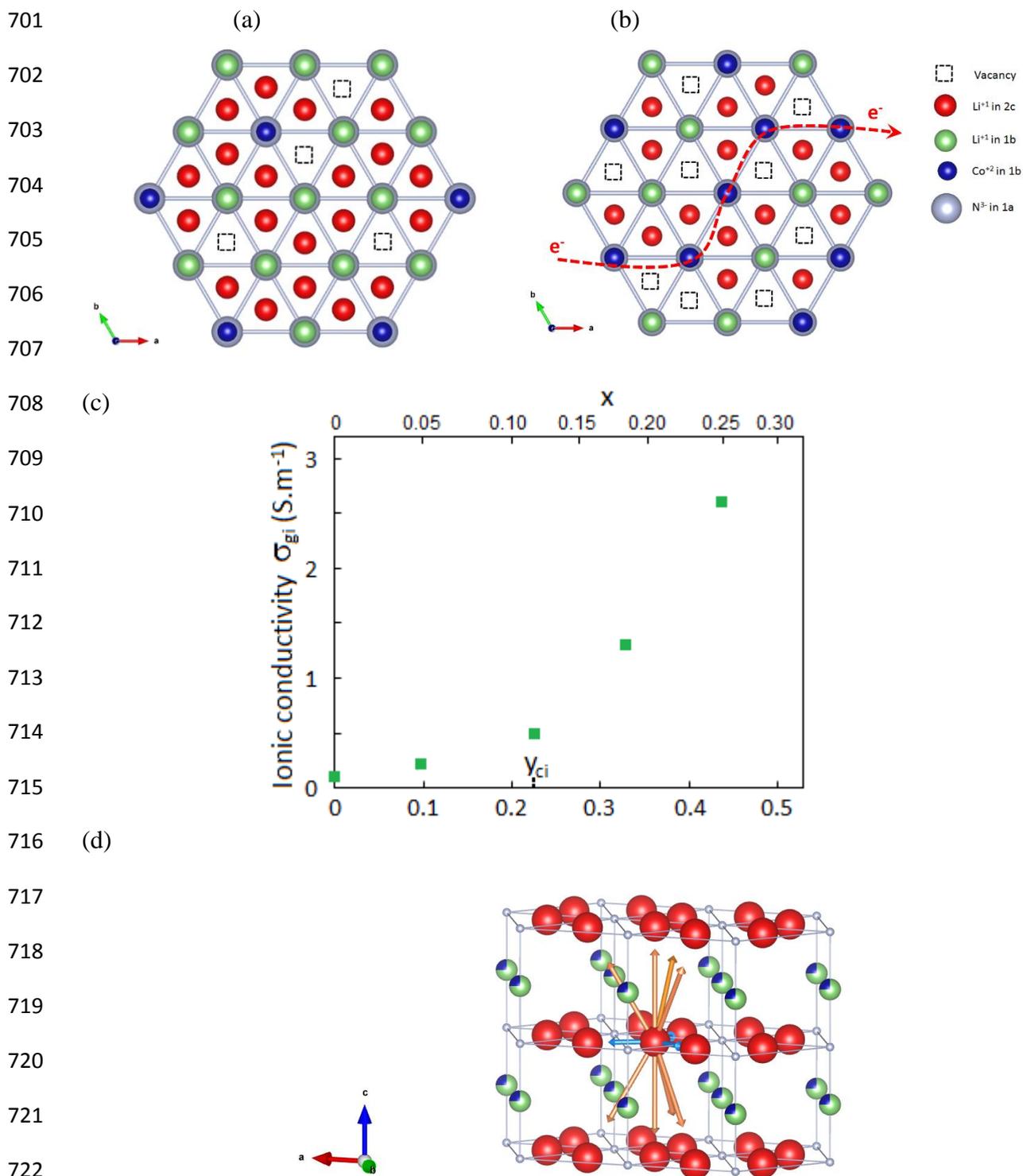


Figure 11.

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