University of Siegen

Li-Argyrodites : Li-ionic Conductivity by Impedance Spectroscopy

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Introduction:

The new ternary Lithium-containing Argyrodite with the formula Li_7PS_6 crystallizes at room temperature in the orthorhombic low temperature modification (isotypic to Cu_7PSe_6), in contrast to the quaternary halide-containing Lithium-Argyrodites $Li_{7-\delta}PCh_{6-\delta}X_\delta$ (Ch = S, Se; X = Cl, I: $\delta \leq 1$; Ch = O, X = Cl: $\delta \leq 1$), which crystallize in the cubic high temperature form of the Argyrodites (space group $F\bar{4}3m$)[1]. The related silver- and copper Argyrodites are known for their good Cu/Ag-conductivities [2,3]. To compare the Li-conductivity of Argyrodites with different compositions, impedance spectroscopic and polarisation measurements were carried out.

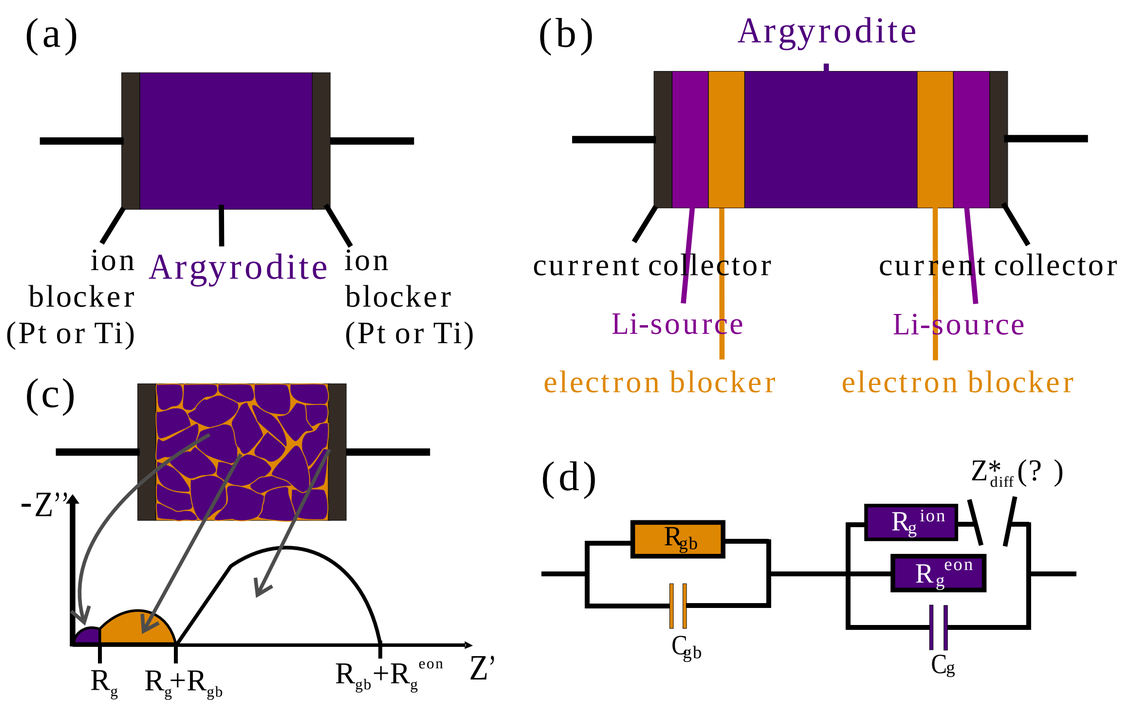
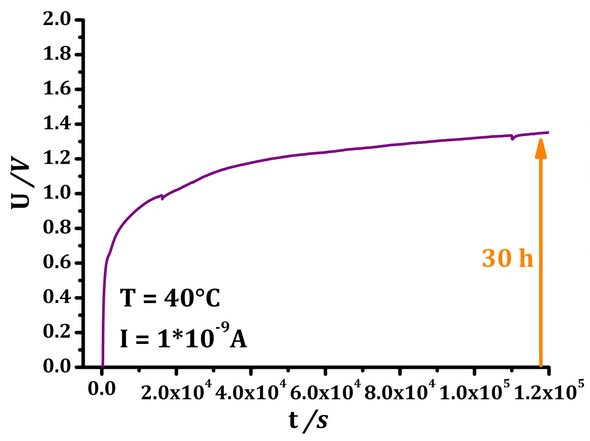


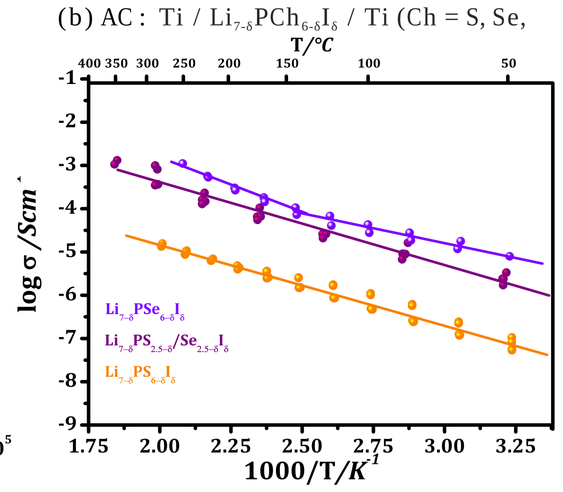
Figure 1:
(a, b) Symmetric cell for electrochemical measurements with (a) ion blocking or (b) electron blocking electrodes
(c) Schematic representation of a cell with a polycrystalline sample pellet and selective ion blocking electrodes and the resulting impedance spectrum
(d) Respective equivalent circuit with the active impedance elements (for electron blockage, Z^*_{diff} is in series with R_g^{eon})
C_g, C_{gb}: bulk-, grain boundary capacitance; R_g, R_{gb}: bulk-,grain boundary resistance; Z^*_{diff}: diffusion

Quaternary Iodoargyrodites $Li_{7-\delta}PCh_{6-\delta}I_\delta$ (Ch = S, Se, S/Se)

(a) DC : Ti / $Li_{7-\delta}PSe_{6-\delta}I_\delta$ / Ti



(b) AC : Ti / $Li_{7-\delta}PCh_{6-\delta}I_\delta$ / Ti (Ch = S, Se,

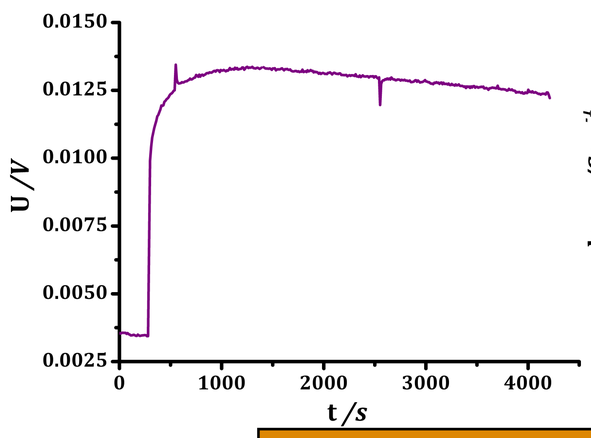


	σ_{all} (T = 40°C) /Scm^{-1}	σ_{all} (T = 200°C) /Scm^{-1}	σ_{eon} (T = 40°C) /Scm^{-1}	E_A /eV
$Li_{7-\delta}PS_{6-\delta}I_\delta$	3.1 * 10^{-7}	1 * 10^{-5}	---	0.38
$Li_{7-\delta}PSe_{6-\delta}I_\delta$	8 *10^{-6}	1.1*10^{-3}	3.4 * 10^{-10}	0.25/0.56
$Li_{7-\delta}P(S/Se)_{6-\delta}I_\delta$	4 * 10^{-6}	1 *10^{-3}	---	0.33

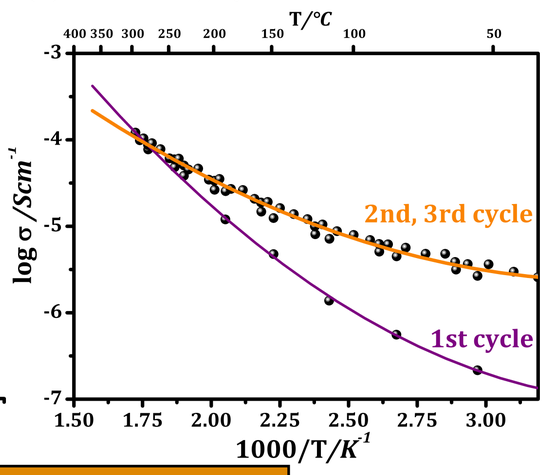
Figure 3:
(a) Wagner-Hebb-polarisation measurements of $Li_{7-\delta}PSe_{6-\delta}I_\delta$ with ion blocking cell arrangement.
(b) Arrhenius plot of $Li_{7-\delta}PCh_{6-\delta}I_\delta$ (Ch = S, Se, S/Se) with ion blocking Ti-electrodes.

Ternary Argyrodite Li_7PS_6

(a) DC : LiAl / $LiClO_4$ / Li_7PS_6 / $LiClO_4$ /LiAl



(b) AC : Pt / Li_7PS_6 / Pt

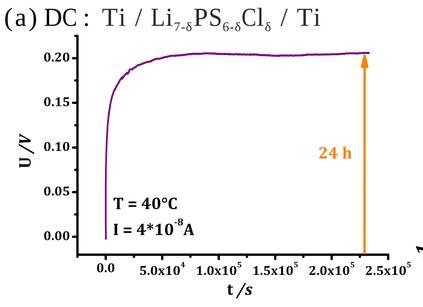


σ_{all} (T = 40°C) /Scm^{-1}	σ_{all} (T = 200°C) /Scm^{-1}	σ_{ion} (T = 40°C) /Scm^{-1}	E_A /eV
2 * 10^{-6}	2.5 * 10^{-5}	---	0.22

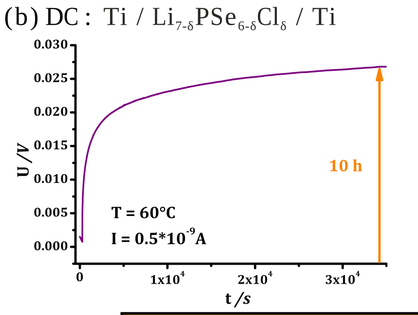
Figure 4:
(a) Wagner-Hebb-polarisation measurement of Li_7PS_6 with electron blocking cell arrangement. The potential is decreasing with time, maybe due to oxidation of free sulphur in the sample.
(b) Arrhenius plot of Li_7PS_6 with ion blocking Pt-electrodes. After the second cycle the loose contacts between electrode / sample and between the grains become closer; the conductivity increases (*Annealing effect*).

Quaternary Chloroargyrodites $Li_{7-\delta}PCh_{6-\delta}Cl_\delta$ (Ch = O, S, Se)

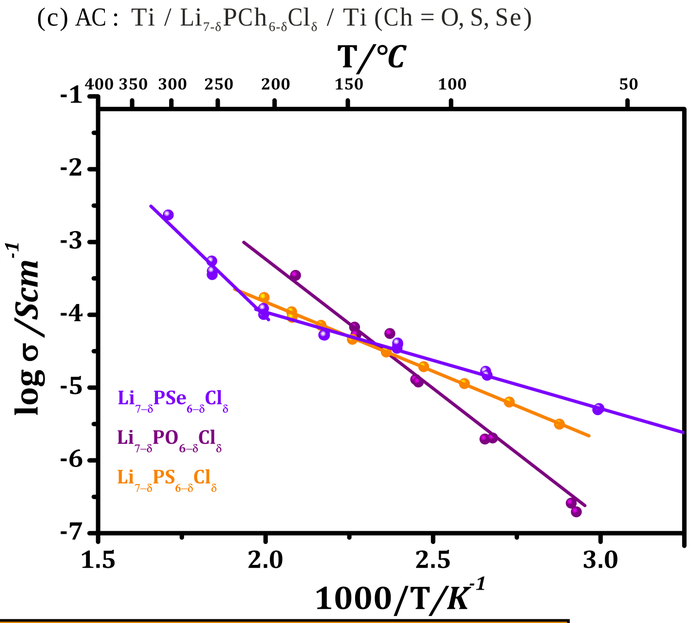
(a) DC : Ti / $Li_{7-\delta}PS_{6-\delta}Cl_\delta$ / Ti



(b) DC : Ti / $Li_{7-\delta}PSe_{6-\delta}Cl_\delta$ / Ti



(c) AC : Ti / $Li_{7-\delta}PCh_{6-\delta}Cl_\delta$ / Ti (Ch = O, S, Se)



	σ_{all} (T = 40°C) /Scm^{-1}	σ_{all} (T = 200°C) /Scm^{-1}	σ_{eon} (T = 40°C) /Scm^{-1}	E_A /eV
$Li_{7-\delta}PO_{6-\delta}Cl_\delta$	5 * 10^{-8}	3.2 * 10^{-4}	---	0.69
$Li_{7-\delta}PS_{6-\delta}Cl_\delta$	2.6 * 10^{-6}	1 * 10^{-4}	1*10^{-8}	0.36
$Li_{7-\delta}PSe_{6-\delta}Cl_\delta$	1 * 10^{-5}	1 * 10^{-4}	7.5 * 10^{-9}	0.26/0.88

Figure 2:
(a, b) Wagner-Hebb-polarisation measurements of $Li_{7-\delta}PCh_{6-\delta}Cl_\delta$ (Ch = S (a) , Se (b)) with ion blocking cell arrangement show fast polarisation due to movement of Li^+. In the polarised state, the measured potential is only due to electronic conductivity.
(c) Arrhenius plot of $Li_{7-\delta}PCh_{6-\delta}Cl_\delta$ (Ch = O, S, Se) with ion blocking Ti-electrodes. For alternating current the kind of blocking is not important, the measured conductivity is the sum of ionic and electronic conductivity.

Sample Preparation:

Li-Argyrodites are highly hygroscopic, therefore all preparative work was done under inert gas atmosphere in an Ar-filled glovebox. Out of the carefully ground samples cylindrical pellets (diameter ø = 6 mm, thickness l = 0.5-3 mm) were prepared by either monoaxial pressing (pressure quaternary Argyrodites: 40kN; ternary Argyrodite: 20 kN) in stainless steel pressing tools or by isostatic pressing (pressure ternary and quaternary Argyrodtites: 250 kN). For ion blockage either discoidal Ti-foil or Pt-paste (coated on sample pellet, annealed for 1h at 500°C) were used as electrodes. For electron blocking the Lithium source was a LiAl alloy, the electron blocker (if present) was chosen to be a mixture of $LiClO_4$ in propylene carbonate with a PE-foil as separator between sample and liquid.

Conclusion:

Electrochemical analysis (impedance and polarisation measurements) show that the new ternary and quaternary Li-Argyrodites exhibit high ionic and low electronic conductivities. The highest Li^+-conductivity is observed for the halogen-containing Selenoargyrodite ($Li_{6.25}PSe_{5.25}I_{0.75}$: around 10^{-5} S/cm at room temperature and 10^{-3} S/cm for 200°C) with an activation energy of 0.25 eV. The electronic conductivity (at T = 40°C) is 10^{-10} S/cm. Surprisingly also the ternary Li-Argyrodites show distinct ionic conductivities (Li_7PS_6: around 10^{-6} S/cm), although crystallizing in the ordered low temperature modification.

Literature and Acknowledgement:

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