Atomically controlled electrochemical nucleation at superionic solid electrolyte surfaces

The atomistic theory of nucleation

The formation of a new phase on a foreign substrate is related to an overcoming of certain thermodynamic barrier $\Delta G(N_c)$, e.g. the nucleation work for creating a critical nucleus consisting of $N_c$ atoms and under certain conditions becomes rate limiting. The nucleation theory (for both classical and atomistic point of view) is based on the Becker-Doering approach treating the nucleation as a sequence of bimolecular chemical reactions where each cluster of size $N$ can be transformed either to a higher or to a lower class by adding or losing an atom, where at equilibrium the rates of attachments and detachments are equal:

$$C_N \xrightarrow{\text{atom}} C_{2N} \xrightarrow{\text{atom}} C_{3N} \ldots C_{eN}$$  \hspace{1cm} (1)

The change of the free enthalpy of formation for a cluster consisting of $N$ atoms can be presented as:

$$\Delta G(N) = N e \Delta \phi + \Phi(N)$$  \hspace{1cm} (2)

where $\Delta \phi < 0$ is the cathodic electrical potential and $\Phi(N)$ is a specific surface energy term accounting for the formation/disappearance of surfaces. At constant volume the form of a nucleus of $N$ atoms can change until the contribution part of $\Phi(N)$ reaches a minimum corresponding to the equilibrium form of the crystal (Gibbs-Curie condition).

For sufficiently large clusters the number of the atoms in the nucleus $\Phi(N)$ and $\Delta G(N)$ can be treated as continuous variables. In this case the term $\Phi(N)$ is expressed by means of specific free surface energy. At a particular voltage $\Delta \phi_c$ the derivative $\partial \Delta G(N)/\partial N$ becomes zero corresponding to the equilibrium condition ($N = N_c$), where the relation between the size of the critical nucleus $N_c$ and the electrochemically induced supersaturation is given by:

$$\Delta \mu = \left[ \frac{d\Phi(N)}{dN} \right]_{N=N_c}$$  \hspace{1cm} (3)

with $\mu$ denoting the electrochemical potential and $\Delta \mu$ representing the electrochemical supersaturation. Equation (3) represents a general form of the Gibbs-Thomson equation. Fulfilling the equilibrium condition the nucleus consisting of $N_c$ atoms can with equal statistical probability disarrange (the nucleus dissolves) or further grow.

For clusters consisting of small number of atoms the macroscopic quantities e.g. specific surface energy lose their physical meaning. $\Delta G(N)$ and $\Phi(N)$ can take only discrete values and the macroscopic theory cannot be applied. In the atomistic model the surface energy term associated with a formation of a configuration of $N$ atoms ($N < 20$) is estimated using the bond energies between the atoms and the substrate $\psi_{a-s}$ and the atoms themselves $\psi_{a-a}$ (the energy term accounting for a substrate induced strain will be omitted for simplicity). These energies are considered to be restricted to the first nearest neighbor and to be equal to the bond energies in a vacuum.
\[ \Phi(N) = N\psi_{\text{kink}} - \sum_{x=1}^{\infty} \psi_{x} \]

Then, equation (2) becomes the form:

\[ \Delta G(N) = Nze\Delta \varphi + N\psi_{\text{kink}} - \sum_{x=1}^{\infty} \psi_{x} \]

where \(\psi_{\text{kink}}\) is the bond energy of an atom in a kink (half crystal) position and \(\sum_{x=1}^{\infty} \psi_{x}\) is the sum of the bond energies of atom(s) in all other positions in the cluster. \(\Delta G(N)\) calculated on the basis of this equation can take only discrete values as shown in Fig.S1.

![Graph showing comparison between classical and atomistic treatment of the nucleation process.](image)

Fig. S1 Comparison between the classical and atomistic treatment of the nucleation process. The free reaction enthalpy change (a) and the change of the electrochemical potential (b) as a function of the number of constituent atoms \(N\) is schematically presented.

By variation of the applied potential one can easily shift the equilibrium towards conditions where the critical nucleus contains one or only few atoms and is stable in a large range of applied potentials (see also Fig.S1).


**S1. Structural characterization of RbAg₄I₅ thin films**

The thickness of the RbAg₄I₅ films was proven for selected samples by cross sectional HRSEM images. Fig S2 shows typical image of thermally evaporated film.

![HRSEM image of a cross section of RbAg₄I₅ film deposited on Ag/SiO₂/Si substrate.](image)

Fig. S2 HRSEM image of a cross section of RbAg₄I₅ film deposited on Ag/SiO₂/Si substrate.

However, the scanning electron microscopy is not appropriate for imaging RbAg₄I₅ because under the electron beam the material fast decomposes and changes its morphology building Ag clusters.

The crystal structure of the deposited films was controlled by XRD measurements.

![XRD diffraction pattern of RbAg₄I₅ film deposited on Ag/SiO₂/Si substrate](image)

Fig. S3. XRD diffraction pattern of RbAg₄I₅ film deposited on Ag/SiO₂/Si substrate
As shown in Fig. S3 the main reflection is of the (110) plane, but also (221) and (311) peaks were detected.

**S3. Conductivity measurements**

The effect of increasing the electronic partial conductivity as a result of Fe-doping of RbAg$_4$I$_5$ was on one hand side essential to enable the STM experiments but on the other hand side the particular value of the electronic conductivity is supposed to be still much lower than the ionic conductivity. To experimentally verify the electronic and ionic partial conductivities in our films we used the Hebb-Wagner polarization technique. It is based on the simple equation:

$$\Delta \varphi = \frac{kT}{e} \ln \frac{a_{Ag}(1)}{a_{Ag}(2)}$$

where $a_{Ag}(1)$ is the activity of Ag at the side of the contact Ag/RbAg$_4$I$_5$ and $a_{Ag}(2)$ is the activity of Ag at the side of the ion blocking (Pt) contact. The initial prerequisite is that the polarization of the electrodes is negligible (non polarisable electrodes). Applying a positive voltage to the Pt electrode, no Ag can dissolve and the steady state current is purely electronic. Knowing the contact geometry the electronic partial conductivity $\sigma_e$ can be estimated$^{1,2}$. It is expected to be independent on the applied voltage (i.e. Ag activity) fixed by the Fe dopant.

If the voltage polarity is reversed mixed ionic and electronic current flows and the total conductivity is measured. The ionic partial conductivity is then calculated from $\sigma_{ion} = \sigma_{total} - \sigma_e$.

Thus, the Ag$^+$ conductivity was estimated to be $\sigma_{ion} = 0.3$ $\Omega^{-1}$ cm$^{-1}$, which is in good agreement with the literature$^3$. The electronic conductivity of doped and undoped RbAg$_4$I$_5$ as a function of the Ag activity is shown in Fig. S4. It demonstrates that $\sigma_e$ of the Fe doped RbAg$_4$I$_5$ is as expected practically independent on the Ag activity and that the $\sigma_e$ of the pure RbAg$_4$I$_5$ is of three orders of magnitude lower (in average). The electronic conductivity of undoped RbAg$_4$I$_5$ is slightly higher compared to the values reported by Bredikhin$^3$ but is within the range of values being already reported$^{3-5}$. However, for thin film measurements the determined partial electronic conductivity was by a factor of 10 higher. This difference we assume is due to possible deviation of the electron donor concentration and/or due to influence of the Pt top electrodes, which may penetrate into the RbAg$_4$I$_5$ films during the RF sputtering. However, as supported by the DFT calculations deviations in the amount of the Fe dopant do not significantly influence the band diagram.
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\[ \frac{\Delta \phi}{kT} = a_{Ag(1)} - a_{Ag(2)} \]

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Fig. S4 Electronic conductivity of Fe-doped RbAg₄I₅ and undoped RbAg₄I₅ measured by Hebb-Wagner polarization technique. The specified \( \Delta \phi \) is the voltage applied to the Pt top electrode (ion blocking for \( \Delta \phi > 0 \)).

References:


S4. DFT calculations of the band gap of pure and Fe-doped RbAg₄I₅

The effect of the electron donor doping in RbAg₄I₅ on the electron density of states was confirmed by DFT calculations at PW1PW hybrid level. The results in Fig. S5 demonstrate the new electron donor levels close to the band edge introduced by the Fe-doping. Without Fe doping the fundamental band gap is calculated as 3.7 eV, which is in good agreement with the reported values¹, ². With additional Fe placed at vacant Ag lattice sites 24e, 24e’ and 8c occupied and unoccupied defect levels appear that are mainly composed of Fe 3d states. These levels decrease the band gap to 1 eV in average.

![Fig. S5 Atom projected density of states at PW1PW level for undoped RbAg₄I₅ (a) and Fe-doped material with Fe on 24e position, (b) 24e’ position, (c) and 8c position, (d). The Fermi level $E_F$ is denoted by vertical bars for spin-up ($\alpha$) and spin-down ($\beta$) electrons.](image)

The influence of the particular site position of the Fe-dopant on the band gap width can be practically neglected.


S5. Determination of the tunnelling barrier height

The tunnelling barrier height was estimated at small voltages (the influence of the tip and sample electronic structures can be neglected) from the current-distance ($I$-$z$) spectroscopy measurements using the equation:

$$\frac{\partial \ln(I)}{\partial z} = -2k = -2\sqrt{\frac{2m_e \Phi_{\text{eff}}}{\hbar}}$$
with \( z \) denoting the tip-sample distance; \( k \) the decay constant; \( m_e \) is the mass of the electron and \( \hbar \) the reduced Planck constant. The effective tunnelling barrier height \( \Phi_{\text{eff}} \) is given by:

\[
\Phi_{\text{eff}} = \Phi - \frac{|eV|}{2} \quad \text{with} \quad \Phi = \frac{\phi_{\text{tip}} + \phi_{\text{sample}}}{2}
\]

where \( V \) is the voltage drop in the tunnel gap and \( \phi_{\text{tip}} \) and \( \phi_{\text{sample}} \) are the work functions of the tip and the sample, respectively. The estimated tunneling barrier values for W and Pt tips are presented in Fig. S6.

![Tunneling barrier height calculated on the basis of the I-z measurements for different voltages](image)

**Fig. S6 Tunneling barrier height calculated on the basis of the I-z measurements for different voltages.**

No significant difference between the W and Pt tip can be observed.

Here the voltage drop in the tunnel gap \( V \) is assumed as equal to the applied voltage \( \Delta \varphi \).

We relate the large standard deviation error to a local variation of the surface properties due to different crystal orientation of the grains and variable properties of the grain boundaries.

**S6. STM imaging of RbAg\(_{4}\)I\(_{5}\) surfaces**

Atomically resolved images of RbAg\(_{4}\)I\(_{5}\) surfaces were measured on different samples with W tips. Mainly (110) and (100) surfaces were detected. The images were typically recorded at positive voltages ranging between 20 mV and 100 mV. However, the STM imaging was performed at voltages up to 500 mV.
Fig. S7 Atomically resolved STM images of RbAg$_4$I$_5$ surfaces recorded with W tip at room temperature. The upper images we assigned to (100) and the lower to (110) faces.

**S7. RbAg$_4$I$_5$ superionic electrolyte**

RbAg$_4$I$_5$ is the most prominent example for fast ion (Ag$^+$) conduction at room temperature. The superionic conductivity was firstly discovered in 1967 by Bradley$^1$ and Owens$^2$ and its crystal structure was resolved the same year by Geller$^3$. Transport properties, defect structure, electrode reactions were intensively studied in the last century$^4$-$^{14}$ and variety of applications were suggested as solid state batteries$^{15}$, acceleration sensors$^{16}$ and resistive switching memories$^{17}$.

References:


