Kinetic Monte Carlo Simulations of Polaronic Diffusion in Titanium Doped Hematite

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Abstract:

Hematite is a promising material for photoelectrochemical water splitting. A key impediment for applications is the slow kinetics of charge transfer caused by the formation of small polarons. It has been experimentally observed that titanium doping enhances the polaron migration, but without a sufficient theoretical model. Here we present a kinetic Monte Carlo model of polaron diffusion, where the influence of dopants is modeled by several different approaches and compared to experimental data.

Polarons:

Quasiparticle formed by the interactions between electrons or holes and lattice ion vibrations

Two types of polarons:
- large non-localized polarons
- small polarons localized in the lattice :
  - mobility (which is less than 1 cm^2/Vs) increases with temperature

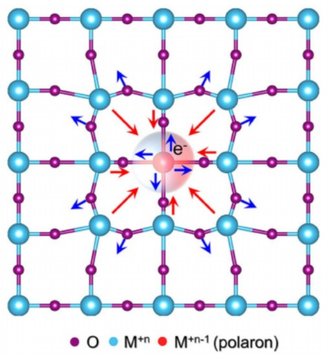


Fig. 1: Charge trapped in the lattice distorts the surrounding atoms [1]

Dopants:

- Creating a defect in the crystal lattice of Fe_2O_3 by substituting iron by titanium significantly increases the mobility of polarons
- The mobility grows with the fraction of titanium in the bulk
- Dopancy [%] – ratio of iron atoms replaced by titanium atoms

Experiment:

- Electrostatic potential induced by injecting approximately 300 electrons into the sample from STM/AFM tip measured a few nanometers away from the surface by Kelvin probe force microscopy
- Procedure of the measurements:
  - Four different samples with 2 %, 0.7 %, 0.03 % and 0 dopancy were prepared
  - 250 to 300 (depending on sample) electrons were injected at temperature 4.7 K
  - The potential remained constant over a few hours after the injection
  - The sample was annealed for 10 minutes and cooled back to 4.7 K to freeze the polarons
  - Several annealing cycles were performed with gradually increasing temperatures

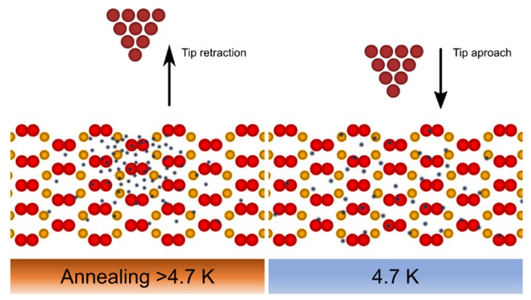


Fig. 2: Experimental procedure

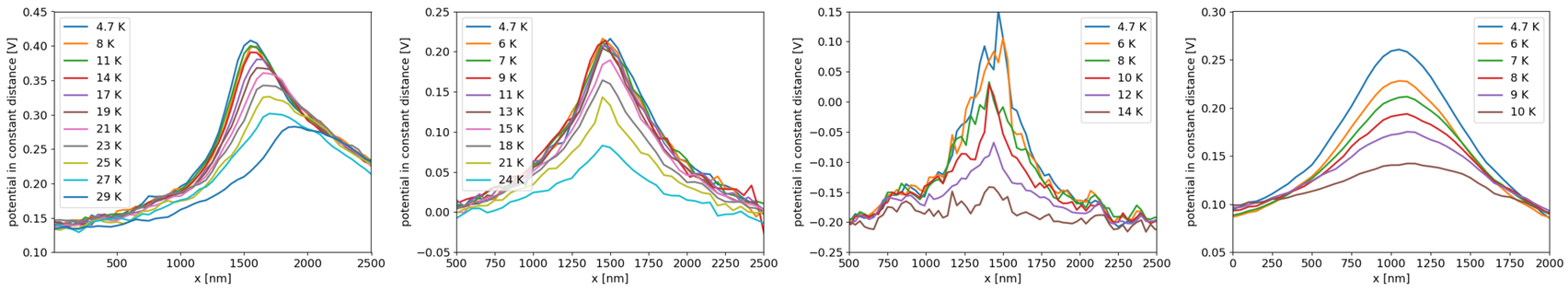


Fig. 3: Measured potential for dopancy = 0 %, 0.03 %, 0.7 % and 3 %

Barrier uniform between every two cells:

Model description:
- The polarons can move in a 3D cubic lattice
- The diffusion barriers between each two cells are set to be the same in the whole domain
- Barriers were fitted from experimental results for 0%, 0.03%, 0.7% and 2 % dopancies
- The outside potential is induce by injection of around 300 electrons (depending on sample)

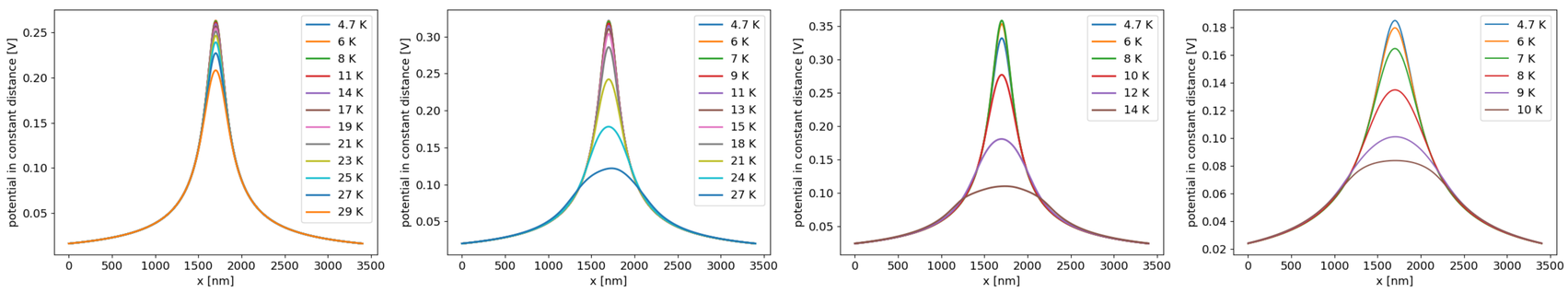
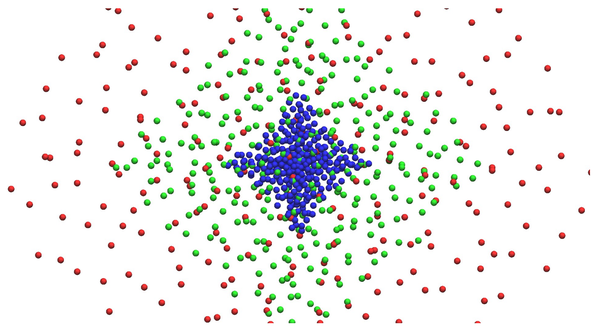


Fig. 4: Simulated potential for dopancy = 0, 0.03, 0.7 and 2 % with uniform diffusion barrier between every two cells



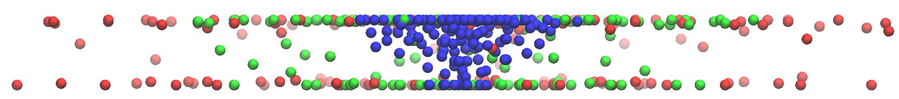


Fig. 5: Top and side view of the spread of the polarons with increasing temperature, blue is after 100 minutes or simulation at temperature T = 4.7K, green after 10 minutes at T = 7 K and red after 10 minutes at T = 8 K

Conclusion:

This approach is able to reproduce the experimental data, however, it is not possible to obtain any closer information about the system than from the experiment.

Dopants included in the domain:

Model description:
- The diffusion barriers the same as in the undoped sample
- Motionless positive charges and the same amount of electrons placed in random locations in the domain, **IP** in Figs 6, 7 denotes potential induced by the distribution of the charges
- Calculation electrostatic force acting on every electron
- In Fig. 7 the barrier was lowered in vicinity of positive charge

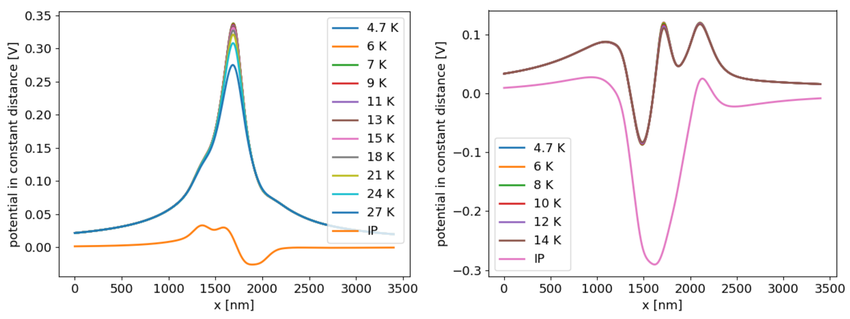


Fig. 6: Barrier constant in the whole domain, dopancies 0.03, 0.7 %

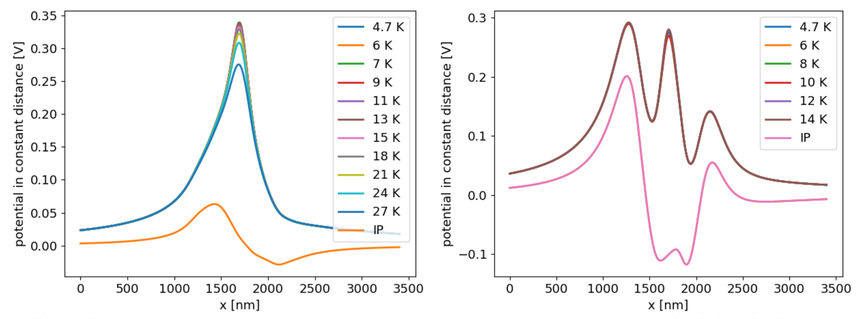


Fig. 7: Barrier lower near dopants, dopancies 0.03, 0.7 %

Conclusion:

This approach is not suitable for this kind of simulations. It yields a nonzero outside potential even without any injected electrons and the decrease of the potential curves with increasing temperature is not fast enough.

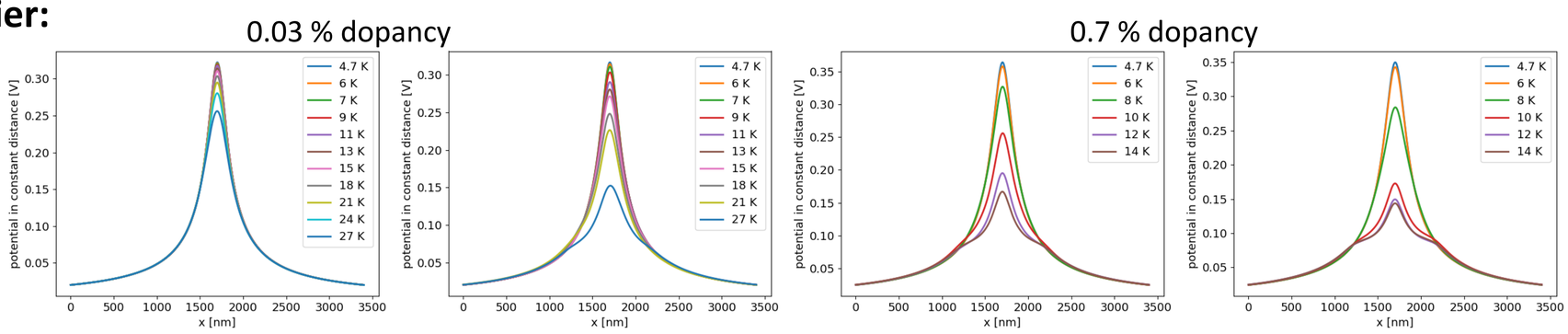
Dopants modeled only by decreased barrier:

Model description:
- The dopants placed into the domain as in the previous case with lowered barriers
- The electrostatic influence of dopants was not considered, only the lowered barriers
- This approach allows to calculate significantly larger areas with lowered barrier

V: Share of number of cells with lowered barrier
r: Sphere radius of area

0.03 % dopancy

0.7 % dopancy



V = 33.1 %, r = 7.07 | V = 41.2 %, r = 7.75 | V = 70.1 %, r = 3.74 | V = 74.5 %, r = 3.87

Fig. 8: Barrier lowered in the whole domain without electrostatic influence of dopants

The initial distribution of positive charges can significantly influence the results. For example for the V = 74.5 %, r = 3.87 case there was higher barrier at place where the electrons were injected. This caused an accumulation of electrons and increased measured potential. Example is shown on Fig. 9.

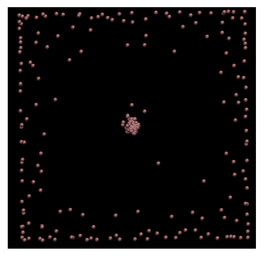


Fig. 9: Example of an accumulation of electrons

References: [1] Y. Natanzon, A. Azulay, Y. Amouyal, *Isr. J. Chem.* **2020**, *60*, 768.