Correlation between mobility enhancement and conformational change in polyaniline and its derivatives: Polaron lattice formation

Yutaka Harima,[a,b*] Fumiyuki Ogawa,[a] Rahul Patil,[c] Xiaoqing Jiang[d]

[a]*Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan*

[b]*Institute for Advanced Materials Research, Hiroshima University, Higashi-Hiroshima 739-8530, Japan*

[c]*Polymer Science and Engineering Division, National Chemical Laboratory, Pune 411 008, India*

[d]*College of Chemistry and Environment Science, Nanjing Normal University, 122 Ninghai Road, Nanjing 210097, P R China*

Abstract

Conformational changes in polyaniline, poly(methylaniline), and poly(methoxyaniline) are studied in perchloric acid and acetonitrile by means of an *in-situ* reflection technique with oxidation level as a parameter. Stretching of polymer chains leading to enhancement of specular reflection at the polymer-coated electrodes is found to be well correlated with the increase in carrier mobility. The concomitant change in mobility and chain conformation observed with the polyaniline family is explained in terms of the formation of polaron lattice at increased oxidation levels.

Keywords: Conformation; Polyaniline; Reflection; Scattering: Mobility

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*Corresponding author. Tel.: +81-82-424-6534; Fax: +81-82-424-5494.
E-mail address: harima@mls.ias.hiroshima-u.ac.jp (Y. Harima).

Introduction

Clarification of conduction mechanisms in molecular solids is a prerequisite for improvement of the device performance since charge transport processes play a crucial role in electronic and optoelectronic devices such as organic light-emitting diodes, organic field-effect transistors, organic solar cells, and so on [1]. Among a variety of molecular solids, conducting polymers are a special class of organic materials in a sense that their conductivities can be varied by many orders of magnitude by chemical or electrochemical doping technique. So far, a number of experimental and theoretical studies have been devoted to the conduction mechanisms in this promising class of organic materials to be utilized in (opto)electronic devices [2].

Polyaniline (PANI) and its derivatives are distinguished from other conducting polymers in that nitrogen atoms make the link between carbon rings and protonation to the heteroatoms greatly affects conductivities with no change in oxidation stage. Because of their unique characteristics, extensive investigations including charge transport studies have been made on PANI and its family [3]. MacDiarmid and Epstein have established a concept of secondary doping, where an importance of polymer chain conformation in the charge transport process is addressed [4]. Static and kinetic aspects of chain conformation in PANI, polypyrrole, and other conducting polymers have been investigated intensively by Otero et al. [5]. Based on the temperature dependence of spin susceptibilities in PANI films, Epstein et al. have claimed the formation of polaron lattice in place of bipolarons to account for reduced susceptibilities at higher oxidation levels and ascribed a tremendous increase of conductivities to the polaron lattice structure. [6]. The polaron lattice model has been subjected to examinations from different standpoints and now becomes well accepted [7].

In our transport study with PANI, mobilities of positive charge carriers were measured as a function of potential, which controls oxidation level defined as the number of charges per monomer unit in the polymer [3e]. A sharp rise of mobility starting at ca. 7% oxidation level was found to be accompanied by a downward deviation in the plot of the spin density vs. oxidation level obtained with an *in-situ* ESR technique. According to the polaron lattice model, electrons are able to flow freely in the partially-filled band and thus have Pauli spins like those in metals. Consequently, it was inferred from this result that the polaron lattice is formed beyond 7% oxidation level. When the polaron lattice structure is established on the polymer chains, on the other hand, a pronounced change in conformation of PANI chains should occur as presumed from the study of MacDiarmid and Epstein [4]. Namely, the formation of polaron lattice would induce both a mobility rise and a stretching of polymer chains simultaneously. To the best of our knowledge, however, a correlation between mobility and chain conformation has never been addressed so far.

In the present work, a reflection technique proposed earlier [8] to *in-situ* survey conformation of polymer chains is outlined and conformational changes in thin films of PANI and its derivatives through the reflected light measurements are studied at different potentials or with oxidation level as a parameter. The observed changes in conformation of polymer chains are compared with mobilities of charge carriers obtained previously and in this study.

1. Experimental

Tetraethylammonium perchlorate (Et_4NClO_4) from Katayama Chemicals and acetonitrile (MeCN) from Tokyo Kasei Co. were purified before use. Aniline from Aldrich, and *o*-methylaniline and *o*-methoxyaniline both from TCI were of reagent grade. They were distilled under Ar atmosphere and stored in Schlenck tubes filled with Ar gas. PANI was grafted on Pt-coated glass plates by a potential-sweep method with 1.3 M aniline in 2.3 M perchloric acid ($HClO_4$). PMA and PMOA films were prepared by cycling a potential between –0.05 and 0.90 V, and -0.05 and 0.85 V at a sweep rate of 100 mV s^{-1} in a 2.3 M $HClO_4$ solution with 0.7 M of *o*-methylaniline and *o*-methoxyaniline, respectively [9]. Electrode potentials were referred to Ag/AgCl/NaCl(satd.). After polymerization, the films were rinsed thoroughly with distilled water, and dried in air. The films were then subjected to dedoping in MeCN/Et_4NClO_4(0.1M) solution at –0.7 V with respect to Ag/$AgClO_4$(0.1 M)+Et_4NClO_4(0.1M). Thicknesses of polymer films used in the reflection measurements were in the range of 1 to 2 μm.

Measurements of charge carrier mobilities in poly(methylaniline) (PMA) and poly(methoxyaniline) (PMOA) films at different oxidation levels were carried out by electrochemistry as described earlier [10]. The mobility (μ) was calculated from the equation $\mu=\sigma/ne$ with the data of conductivity (σ) and carrier density (n) determined simultaneously with the *in-situ* conductivity measurement and potential-step chronocoulometry, respectively. The *in-situ* reflection technique with a He-Ne laser (633 nm) is described in our previous paper [8]. The optical arrangement is schematically illustrated in Fig. 1, where the polymer-coated electrode is slightly tiled from the two parallel glass plates in order to avoid a light reflected directly at the front glass surface. A current signal from a Si photodiode was converted to voltage using a current/voltage amplifier and the voltage signal was fed to a lock-in amplifier. Reflection measurements were made with PANI, PMA, and PMOA films grafted on Pt/Cr-coated glasses in MeCN/Et_4NClO_4(0.1M) and $HClO_4$(pH 1) solutions. The thin Cr underlayer (1 nm) is employed to enhance an adhesion of a Pt layer on glass plate. Reflected light intensities were measured as a function of potential together with measurements of oxidation levels of the polymer films as follows: The potential of a polymer electrode was kept at a sufficiently negative potential where the polymer film is of a leucoemeraldine form. The potential was stepped to a given potential where an oxidation (doping) process occurs. The reflected light intensity changed with time and reached finally a constant value as shown in Fig. 3 of ref. 10. The steady-state value was taken as the reflected light intensity at the stepped potential. Currents flowing during the potential step were integrated by use of a coulometer to evaluate the oxidation level of the polymer film at this potential value. Subsequently, the potential was stepped back to the initial value and the amount of electricity for the cathodic process was measured to confirm reproducibility of the doping/dedoping process. After keeping the polymer film at this potential for, normally, more than ten minutes till the reflected light intensity was recovered to its initial value, the potential was stepped again to another potential slightly more positive than the previous one. This procedure was repeated and the reflected light intensities were measured as a function of potential or oxidation level. The oxidation level defined as the number of charges per monomer unit was evaluated by measuring the weight of the completely dedoped polymer film after the experiment.

2. Results and discussion

Projected images of a 633-nm light reflected at a PANI film are represented in Fig. 2, where a thick tracing paper replaced with a slit in Fig. 1 is used as a projection plane. The cyclic voltammogram of the same PANI film electrode is included in the middle of the figure. When the PANI film is completely reduced at -0.2 V, a hazy red light is spread over the projection plane with no light spot. The light spot appears at 0 V and becomes clear with an increase in potential. However, it tends to reduce its intensity as the applied potential is made more positive than the first oxidation peak at 0.2 V. At potentials beyond 0.4V, neither light spot nor hazy red light is seen and no light reaches the projection plane. Such a change in the projected image with the applied potential is reproducible and a similar observation is made also with PMA and PMOA films in addition to the PANI film. In our preceding paper [8], the potential change of the reflected light intensity has been explained reasonably as below. In the reduced state of the PANI film where polymer chains have a coiled structure [4], a light scattering or a diffuse reflection takes place in the polymer layer and thus a negligible intensity of light reaches the photodetector placed at a right position of specular reflection. By increasing the potential, polymer chains stretch and the coiled structure relaxes as has been demonstrated by MacDiarmid and Epstein [4]. Consequently, Rayleigh or Mie scattering is attenuated in the polymer film and the incident light can go deep into the polymer layer to reach a highly reflective Pt surface. Then, specular reflection at the Pt surface occurs effectively and the reflected light gains its intensity. In accord with this view, it has been reported that PANI particles of 4 to 5 μm in average diameter large enough to scatter a visible light are found in its reduced state and they disappear in the oxidized state [11]. When the potential is raised further, the PANI film turns a blue-black color. At these potentials, therefore, the PANI film starts to absorb the incident 633-nm light and the intensity of light coming to the Pt surface reduces. Absorption of the 633-nm light due to the heavily oxidized PANI layer is responsible for fadeaway of the light spot at potentials beyond 0.3 V. For clarification, the events that occur in the polymer film at three different oxidation stages, i.e., a) completely reduced, b) oxidized, and c) heavily oxidized states, are schematically depicted in Fig. 3. Based on the reflection technique, therefore, expansion or shrinking of polymer chains resulting from a conformational change can be detected sensitively as a function of oxidation level of a polymer film.

Fig. 4 compares dependencies of reflected light intensity and mobility on oxidation level for PANI in $HClO_4$ and $MeCN/Et_4NClO_4$. The mobility varies with oxidation level in a fairly complicated manner, but both of the mobility plots are quite similar in solutions containing ClO_4^- as a common dopant, implying that the electrochemically determined mobilities represent properties of PANI itself, being not affected by the solvent [3d]. The variation in mobility for PANI films in MeCN/Et_4NClO_4 was investigated later on the bases of ESR and optical absorption measurements [3e], and the same explanations may apply to PANI in $HClO_4$. It seems to be necessary here to review the results and interpretations for the mobility plots briefly.

In an oxidation range up to 7%, the spin number increased in proportion to the number of charges removed from the PANI film, suggesting an exclusive generation of isolated polarons. An initial decrease of mobility followed by a small hump is seen in this region where only polarons prevail in the film. The rather complicated mobility change for the PANI film in the low oxidation region was attributable in part to a change in the film structure caused by incorporation of bulky anions into the film. This reasoning may also apply to the initial mobility changes for PMA and PMOA in MeCN and $HClO_4$ shown in Figs. 5 and 6. Another common feature to be noted in the mobility plots of Figs. 4 to 6 is relatively high polaron mobilities of the order 10^{-4}-10^{-3} $cm^2\ V^{-1}\ s^{-1}$ compared with those for electrochemically synthesized polythiophene and poly(3-methylthiophene) [9,12]. The high polaron mobilities for the PANI family still remain a matter of debate. When the oxidation level is increased beyond 7%, a sharp rise of mobility is noted in Fig. 4. It was from this oxidation stage that the double logarithmic plot of spin number (N_s) vs. oxidation level started to deviate downward from a straight line of a unity slope and the ESR linewidth started also to increase [3e]. Earlier, the downward deviation of the N_s plot was the point of controversy and two different explanations were proposed, i.e., formation of polaron lattice or generation of diamagnetic bipolarons like in other conducting polymers [6,13]. Our previous study with poly(3-methylthiophene) has demonstrated that the evolution of bipolarons at oxidation level as low as 0.4% led to a mobility increase and a decrease in the ESR linewidth [14]. In case of PANI, on the contrary, the linewidth was increased along with the downward deviation of the N_s plot. In accord with the view of Epstein et al. [6], we interpreted the deviation in the N_s plot in terms of the conversion of Curie to Pauli spins. The increase in linewidth on change from Curie to Pauli spins is reasonable since it is ascribed to faster relaxation associated with higher mobility of Pauli spins at the Fermi level.

Our main concern in this study is a change of reflected light intensity with oxidation level. As shown in Fig. 4, the reflected light is very weak and constant at oxidation levels below several percents, especially in MeCN solution. This implies that the PANI film in this oxidation region consists of a coiled structure that scatters an incident light beam effectively. It is to be noted that the light intensity is kept almost constant in this region although the mobility of paramagnetic polarons goes down and up. This illustrates that expansion of PANI film due to incorporation of ClO_4^- responsible for the initial variation of mobility does not bring about a change in reflected light intensity. It is seen from Fig. 4 that when the oxidation level is greater than ca. 5%, the light intensity sharply rises in both solutions, suggesting a transition in polymer chain conformation from a coiled structure to a stretched polaron lattice structure. We note readily and clearly that the onset oxidation level for the increase in light intensity is in good agreement with the oxidation level from which the mobility jumps up in both $HClO_4$ and MeCN solutions. This is what we have expected in the Introduction and the observed coincidence validates our speculation. The decline of the light intensity beyond ca. 20% oxidation level, shown in Fig. 4a and b, is due to coloration of the PANI film as explained in Fig. 3c.

In order to generalize our conclusion on PANI, two derivatives of PANI, i.e., PMA and PMOA, were examined. Figs. 5 and 6 represent plots of light intensity and mobility for PMA and PMOA, respectively. These plots were also obtained in $HClO_4$ and $MeCN/Et_4NClO_4$ solutions. As for PMA, the mobility is varied in two steps like that for PANI, although the extent of the mobility increase is small compared with that for PANI shown in Fig. 4a. The second-step increase of mobility for PMA in both solutions starts at around 10% oxidation level. In $HClO_4$, on the other hand, the reflected light intensity starts to increase slightly at 1% oxidation level, but a marked increase occurs almost at the oxidation level where the mobility increase is observed. In case of PMA in MeCN shown in Fig. 5b, it seems that the conformational change takes place at oxidation level for the first mobility rise rather than the second one. For PMOA in $HClO_4$ and MeCN shown in Fig. 6, changes of mobility in the low oxidation region are slightly different from those for PANI and PMA in a sense that the first-step increase of mobility is not observed. However, the mobility increase is clearly seen in $HClO_4$ and MeCN at around 10% oxidation level, corresponding fairly well to the onset of the conformational change.

On the basis of good correlations between changes in mobility and reflection observed with the PANI family, it is reasonable to conclude that the polaron lattice formation is responsible for the enhancement in both mobility and stretching of polymer chains, the latter leading to the increase in the reflected light intensity.

3. Conclusions

Conformational changes with oxidation level are studied with PANI, PMA, and PMOA by using an *in-situ* reflection technique in protic and aprotic solvents. The results are compared with the mobility data obtained earlier and in the present work. It is found that the formation of polaron lattice resulting in a stretching of polymer chains well as the increase in mobility takes place at 5-10% oxidation level in thin films of the PANI family.

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Figure captions

Fig. 1. Schematic illustration of an optical arrangement for the reflection measurements.

Fig. 2. Projection images of a He-Ne laser beam reflected from a PANI-coated Pt electrode biased at different potentials in $HClO_4$(pH 1). A CV curve of the PANI film in the same solution is included.

Fig. 3. Proposed mechanisms for a light reflection on PANI film at a) reduced, b) oxidized, and c) heavily oxidized states.

Fig. 4. Plots of (○) reflected light intensity and (□) carrier mobility against oxidation level for PANI in a) $HClO_4$(pH 1) and b) MeCN/Et_4NClO_4(0.1 M). Mobility plots are cited from ref. 3d. Broken lines are a guide for eyes.

Fig. 5. Plots of (○) reflected light intensity and (□) carrier mobility against oxidation level for PMA in a) $HClO_4$(pH 1) and b) MeCN/Et_4NClO_4(0.1 M). A mobility plot of Fig. 5a is cited from ref. 9. Broken lines are a guide for eyes.

Fig. 6. Plots of (○) reflected light intensity and (□) carrier mobility against oxidation level for PMOA in a) $HClO_4$(pH 1) and b) MeCN/Et_4NClO_4(0.1 M). A mobility plot of Fig. 6a is cited from ref. 9. Broken lines are a guide for eyes.

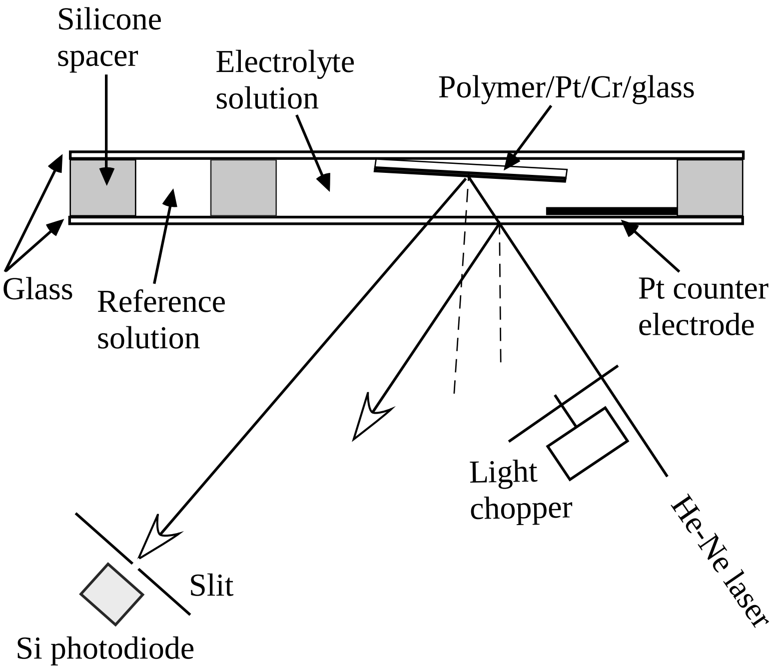
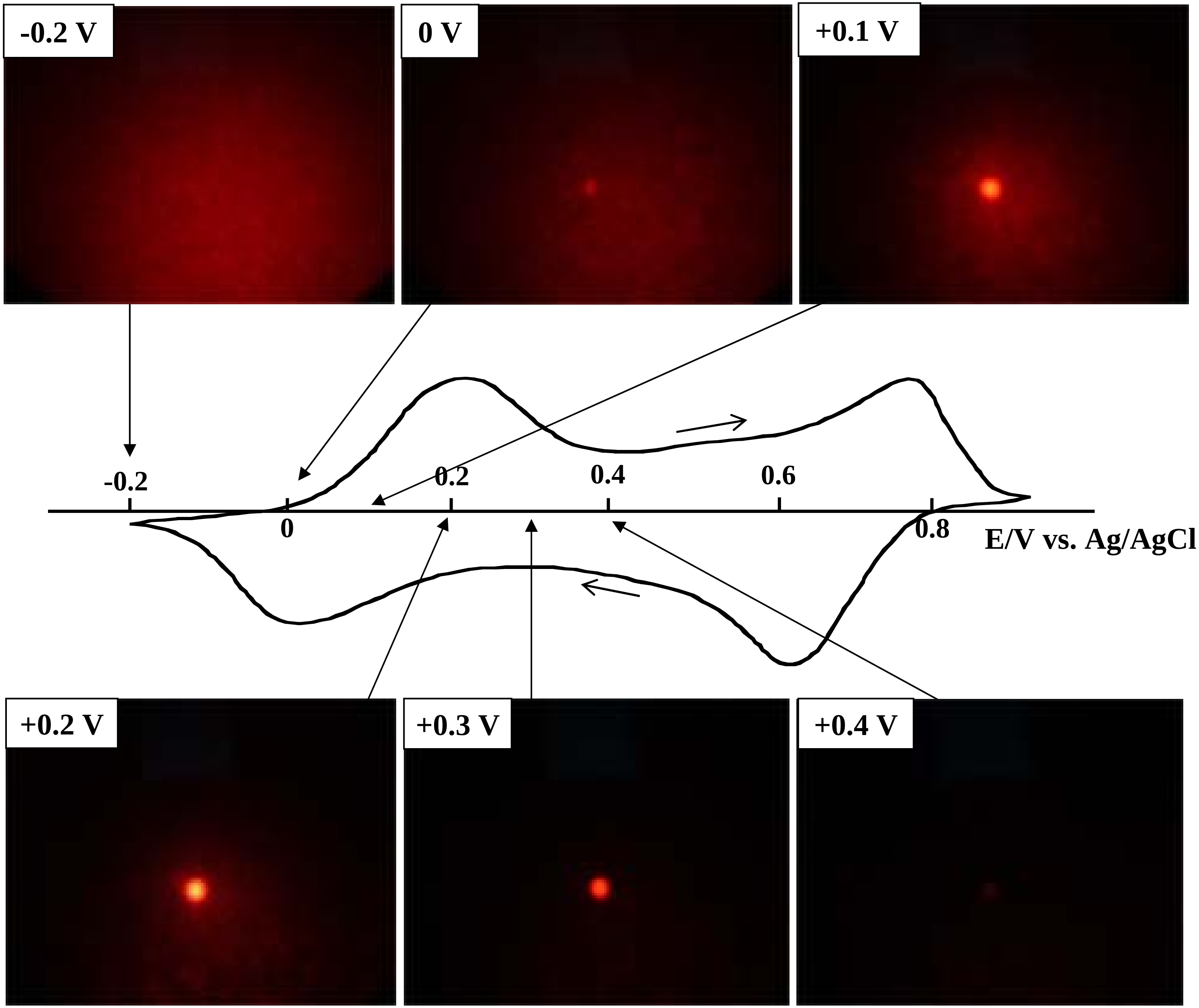


Fig. 1, Harima et al.



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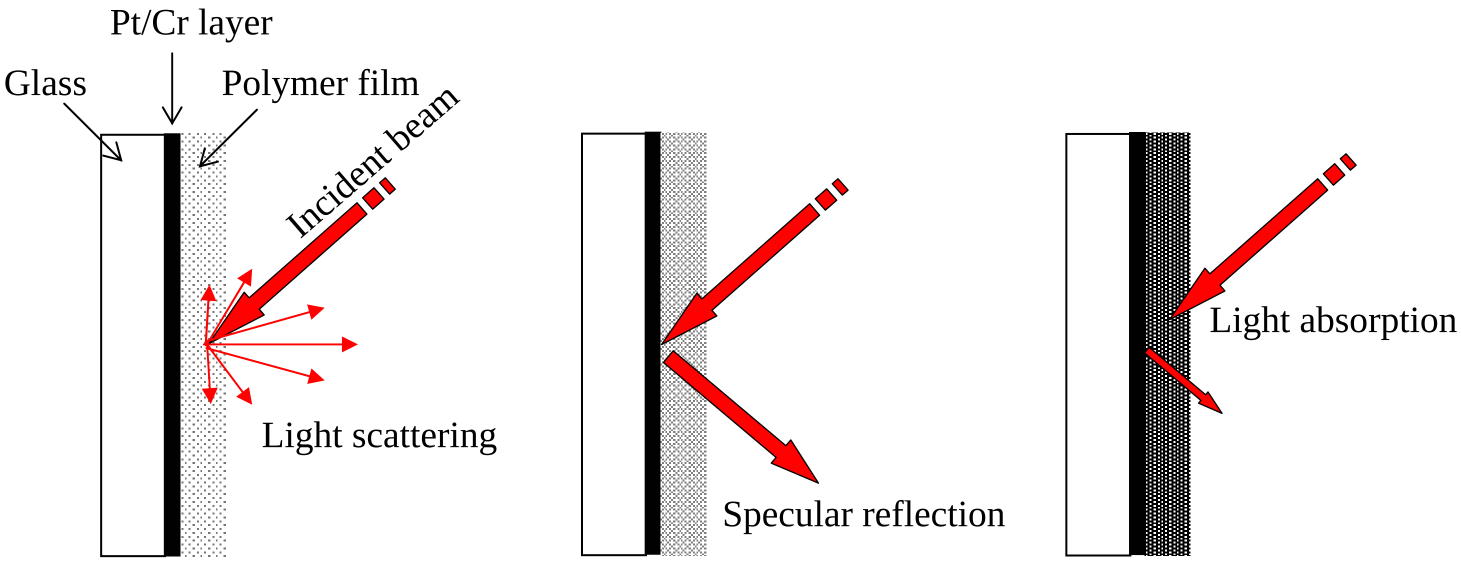
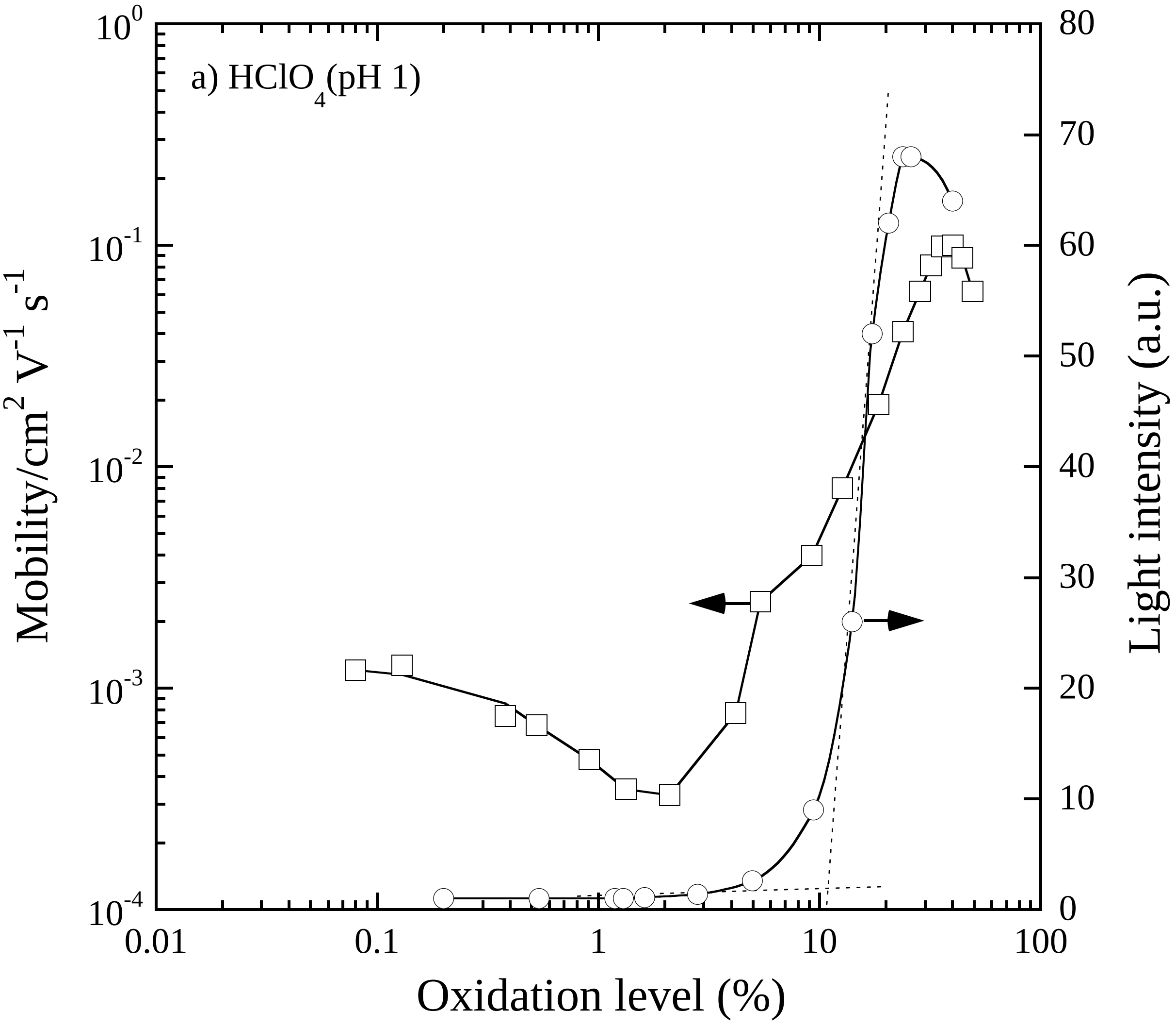


a) Reduced state b) Oxidized state c) Heavily oxidized state

Fig. 3, Harima et al.



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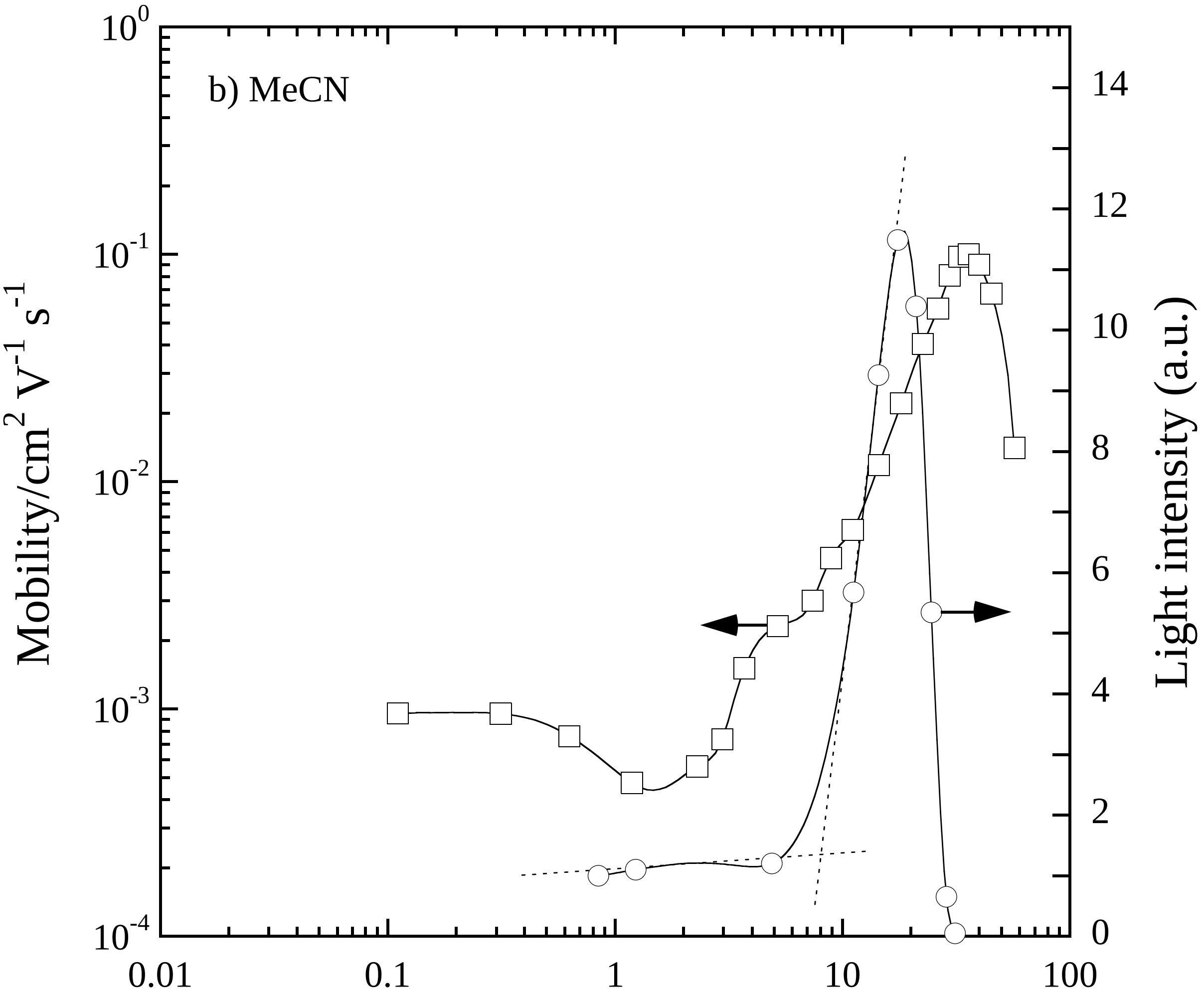
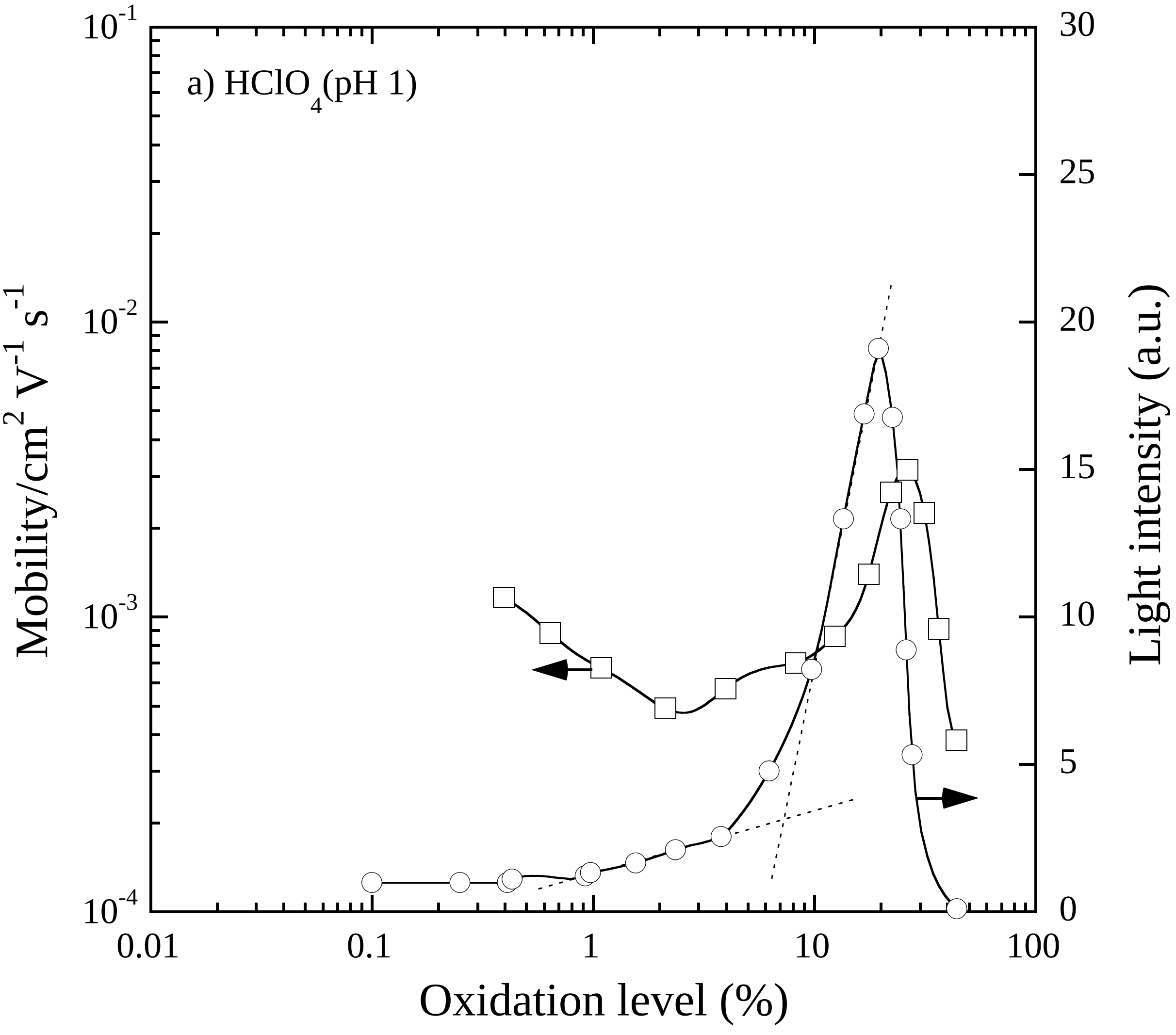


Fig. 4b, Harima et al.



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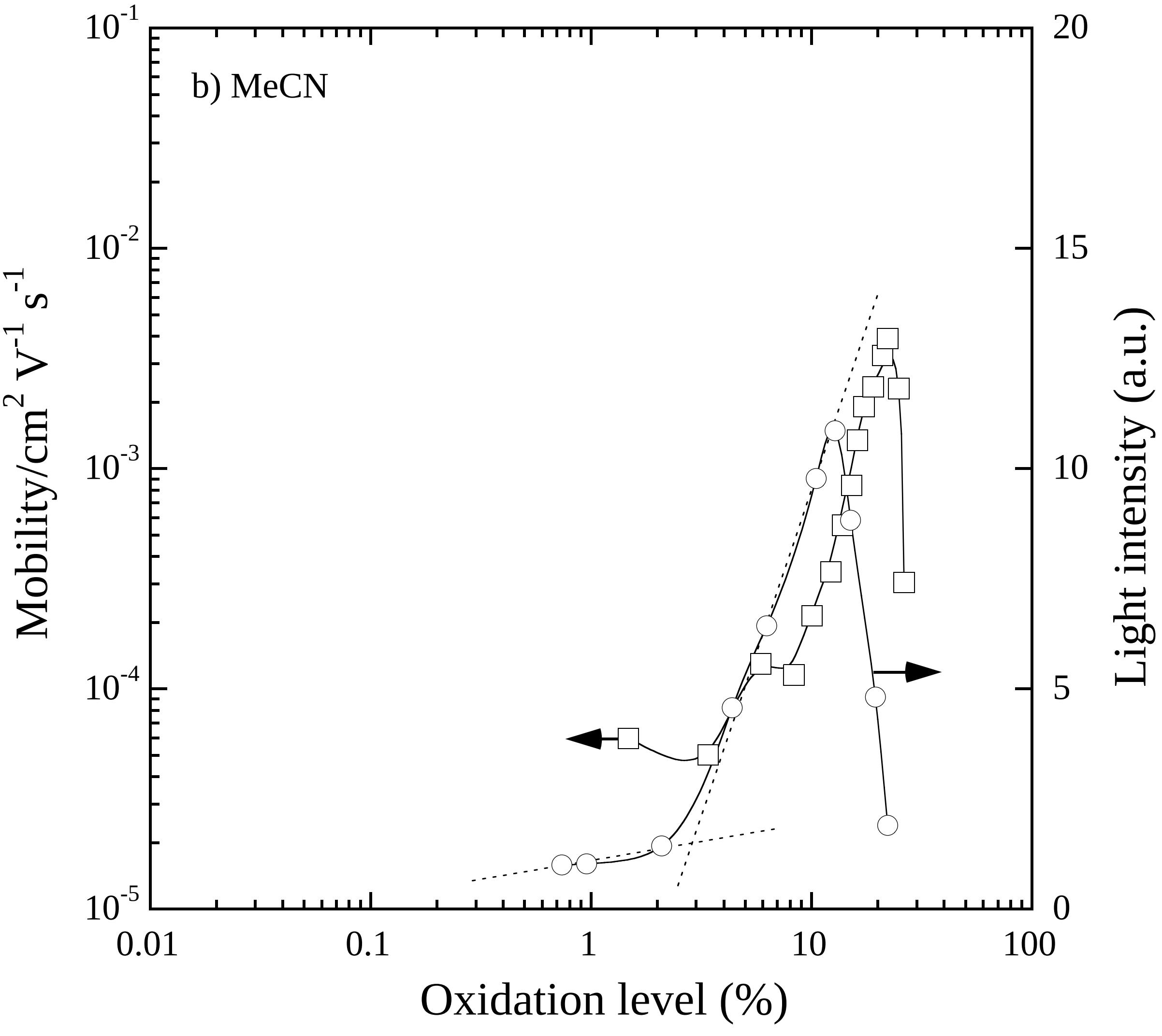

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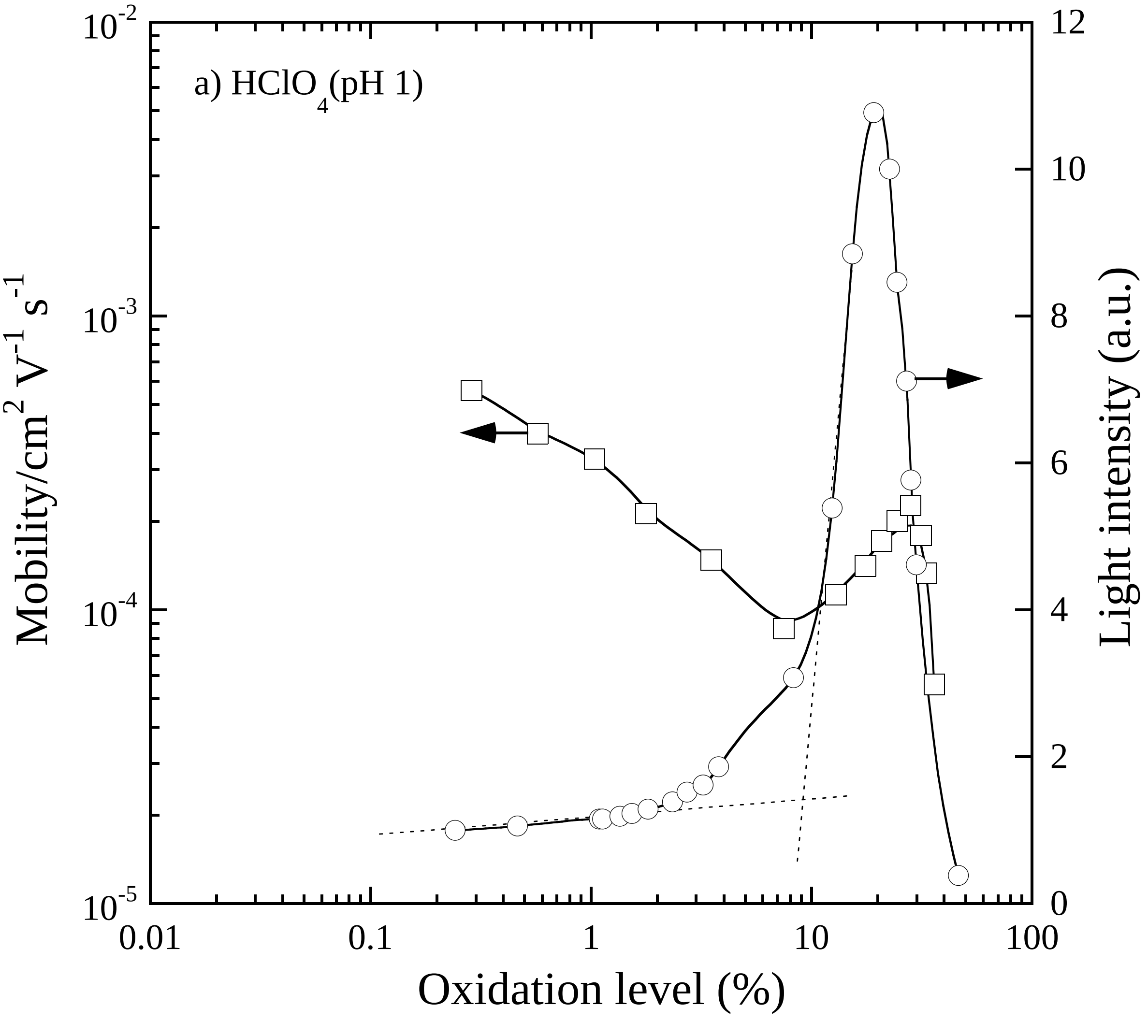

Fig. 6a, Harima et al.

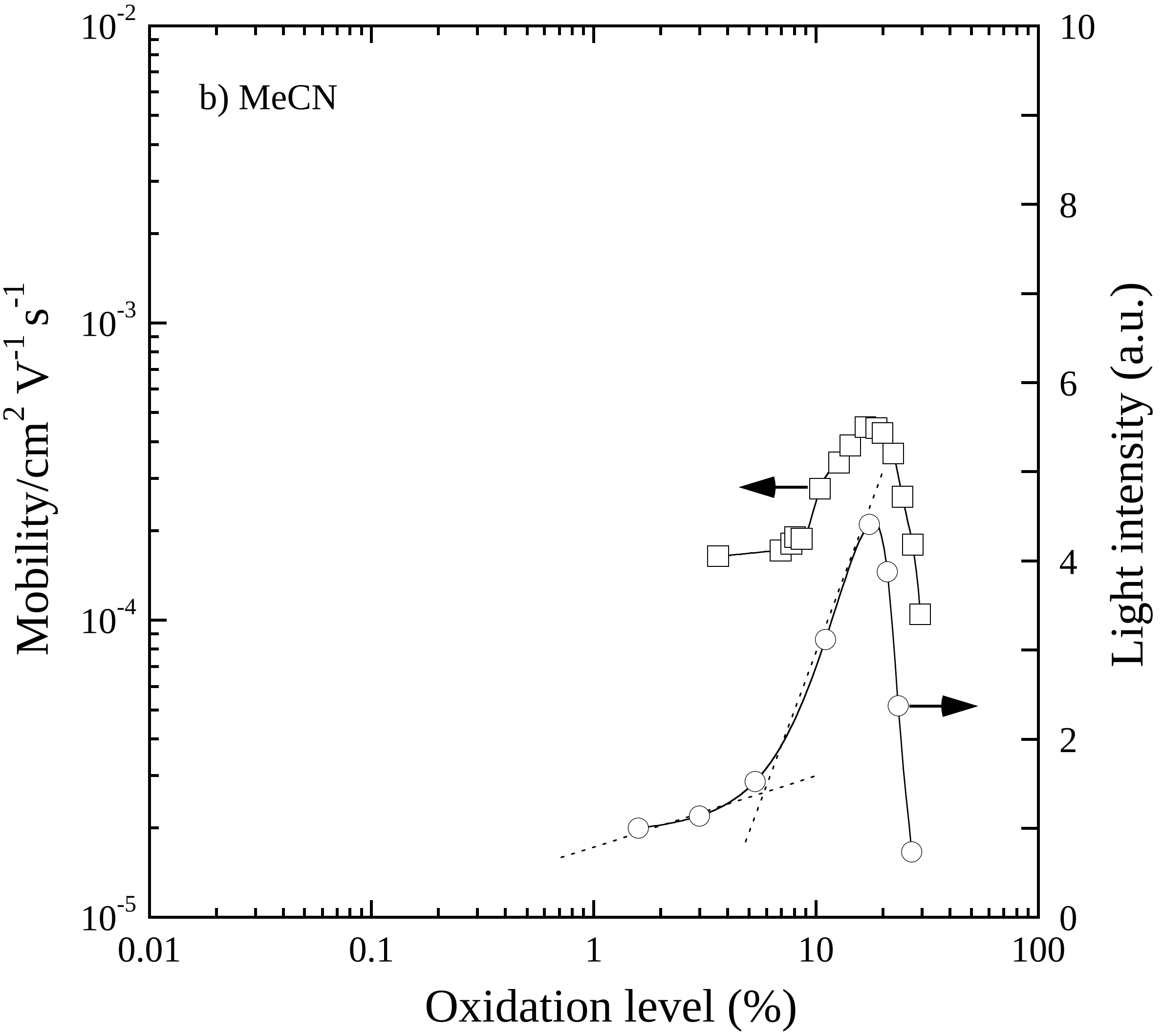

Fig. 6b, Harima et al.