



HAL
open science

Internal Charge Accumulation and Chemical Analyses of Fluorinated Polymer Irradiated by Proton

Kaisei Enoki, Kazuki Endo, Kaoru Ueda, Hiroaki Miyake, Yasuhiro Tanaka,
Virginie Griseri, Gilbert Teyssedre, Yusuke Daiko

► **To cite this version:**

Kaisei Enoki, Kazuki Endo, Kaoru Ueda, Hiroaki Miyake, Yasuhiro Tanaka, et al.. Internal Charge Accumulation and Chemical Analyses of Fluorinated Polymer Irradiated by Proton. 2021 IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP), Dec 2021, Vancouver, France. pp.659-662, 10.1109/CEIDP50766.2021.9705357 . hal-03580920

HAL Id: hal-03580920

<https://hal.science/hal-03580920>

Submitted on 18 Feb 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Internal Charge Accumulation and Chemical Analyses of Fluorinated Polymer Irradiated by Proton

Kaisei Enoki¹, Kazuki Endo¹, Kaoru Ueda¹, Hiroaki Miyake¹, Yasuhiro Tanaka¹,
Virginie Griseri², Gilbert Teysse², Yusuke Daiko³

¹ Tokyo City University, Tokyo, Japan

² Laplace, University of Toulouse, CNRS, INPT, UPS, France

³ Nagoya Institute of Technology, Aichi, Japan
g2191001@tcu.ac.jp

Abstract- The number of satellites operated in an environment in which exist high-energy protons is currently increasing. Therefore, the investigation of the impact of protons on the insulation properties of materials is important. In this work, we investigate the relationship between charge accumulation phenomena and modification of molecule structure by proton irradiation. We focus on ETFE (ethylene tetrafluoroethylene copolymer) used at wire harness irradiated by proton and measured the space charge distribution using the PEA method during the proton irradiation. Furthermore, we investigated the modification of the molecular chain using x-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance (NMR). As the result, we observed that the molecule chain is scissored by proton irradiation. These phenomena can be considered as one of the reasons for charge accumulation.

I. INTRODUCTION

Many satellites are used in several kinds of orbits for telecommunications, environmental observation, resource exploration, the global navigation satellite system (GNSS), and social security [1]. Their surfaces are made with many insulating materials such as the multi layer insulator (MLI), optical solar reflector (OSR), coating material of wire harness, and so on. Spacecrafts are operated in the radio-active rays environment, such as high energy electrons and protons. Charged particles accumulate in the bulk or the surface of materials of spacecraft and lead to electrostatic discharge (ESD) phenomena [2]. ESD is the origin of satellite anomalies; hence, we should investigate charge accumulation phenomena in the bulk of satellite surface materials [3].

Currently, the demand for the use of GNSS is continuously increasing for autonomous driving cars application as example. These satellites are operated in the Van Allen radiation belt and there are high energy protons. Furthermore, exploration of the moon and other planet plans, such as ARTEMIS and Luna plans are centrally drawn up by the USA, EU, and Russia. However, these environments are outside the earth's magnetosphere where solar protons with high energy and wide energy range are irradiated. Therefore, to prevent accidents and ensure the high reliability of satellite operations, it is essential to investigate the charging and discharging characteristics of surface materials of satellites exposed to protons [4].

We focus on ETFE (ethylene - tetrafluoroethylene copolymer), which is used for coating material of wire harness.

In this paper, we measured the space charge distributions under proton beam irradiation to investigate the charging and discharging characteristics. Furthermore, for understanding the relation between charge accumulation phenomena and modification of molecular structure by the proton irradiation, we investigated the modification of the molecular chain using x-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance (NMR).

II. EXPERIMENTAL CONDITIONS

A. Sample Treatment

We focused on ETFE (Fluon®, manufactured by AGC Inc.). Figure 1 shows the molecular chain of ETFE. "m" and "n" are component ratios. For the experiments, a sample thickness of about 100 μm was used. The sample used for the space charge measurement during proton irradiation has an Al evaporated layer on both sides of the sample. During proton beam irradiation, the both Al evaporated layer was connected to the ground. When we measured the molecular bonding energy, we used the proton-irradiated sample after 1 day, without previous metallization.

B. Irradiation facility and conditions

The irradiation was carried out using the 3 MV Tandem Accelerator facility of Takasaki Advanced Radiation Research Institute of the National Institutes for Quantum and Radiological Science and Technology, Japan (its former name was the Japan Atomic Energy Agency). The proton beam irradiation was carried out in a vacuum of approximately 1×10^{-5} Pa. The acceleration energy of the irradiated proton was 2.0 MeV with a current density of 30 nA/cm². The irradiation time was 30 min. The irradiation area was 30 x 30 mm². The

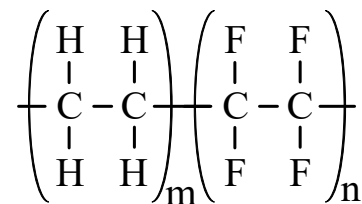


Fig. 1. Molecular chain of ETFE

calculated penetration depth of irradiated proton is about 51 μm using the stopping and range of ions in matter (SRIM) at the above irradiation conditions [5].

C. PEA measurement principle and conditions

The PEA method provides the space charge density distribution in the bulk of dielectric materials. As the detail of the principle of the PEA method was already described in many past papers, please refer for example to [6-8] for general aspects. Figure 2 shows the schematic diagram of the PEA method for in-situ space charge measurement during charged particle irradiation. The ring electrode is used as the electrode on the irradiation side, and the irradiated particles reach the sample directly. The ring electrode is connected to the Al layer. We used an adhesive to stick the sample to the ground (GND) electrode. No DC field was applied during irradiation and space charge measurement. Measurement times are 60 min (30 min during irradiation and 30 min for relaxation) and we measured space charge distribution every 10 seconds.

D. XPS measurement conditions

SSX-100 (from Surface Science Instruments) was used to obtain XPS spectra at Tokyo City University Nanotechnology Research Center. The source of X-ray is Al $K\alpha$ type anode (1487 eV) and the detecting energy range is 0 – 1100 eV with 0.58 eV of FWHM. We measured the C_{1s} spectrum at the irradiation surface side of the sample.

E. NMR measurement conditions

Solid state NMR measurement was carried out using a Jeol Resonance ECA600II spectrometer. The NMR spectra were measured at 600 MHz, 1.5 s of decay time between pulses, and MAS spinning rate of 20 kHz. We used 3.2 mm MAS probe to measure ^1H . A sample of 30 x 30 mm (irradiation area) was cut into required standard pieces for measurement.

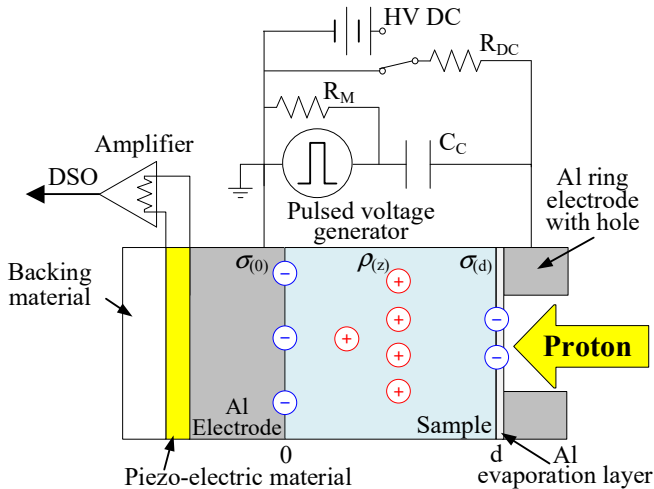


Fig. 2. Schematic diagram of the PEA method for charged particle irradiation

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. Space charge distributions measurement

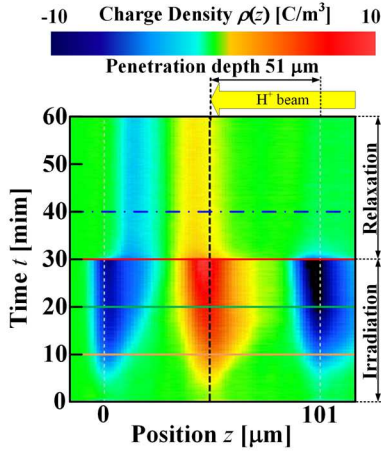
Figure 3 shows space charge distribution under proton irradiation. Figures (a), (b), (c), and (d) show the space charge behavior with time, the space charge distributions, the electric field distributions, and the accumulated positive charges in the material with time, respectively. In those figures, the irradiation surface is shown at the right side, and the vertical black broken line in the sample is the calculated penetration depth of the irradiated proton. For simplicity, “irradiation area (IA)” is the range from the irradiation surface to the calculated proton penetrated depth and the “non-irradiation area (NIA)” is the range from the penetrated depth to the left side grounded electrode.

From Fig.3(a), (b), we can see positive charge accumulation at the calculated penetration depth of irradiated protons. Furthermore, negative charges were injected at the NIA from the GND electrode over time. From Fig. 3(c), the maximum value of the electric field at NIA is 8 kV/mm. We have already shown that charge injection was not observed at so low electric field in DC conditions [9]. From Fig. 3(a), (b), we can see positive charge accumulation at the NIA, even more clearly during the relaxation time. This feature can be due to transport from irradiated layer. The injection of negative charges and transport of positive charges possibly result from higher electric field than determined in the IA.

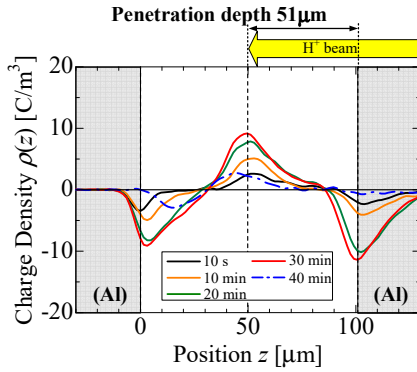
From Fig. 3(d), it can be seen that the increasing trend of the amount of positive accumulated charge changes 17 minutes after the start of irradiation. Furthermore, the maximum amount of positive stored charge is about 0.24 mC/m^2 . However, the irradiation current density is 30 nA/cm^2 , which corresponds to 0.3 mC/m^2 at every 1 s. It can be found that this charge storage is very low. It is thought that this is because the negative charge is injected into the sample and transported into the sample due to the internal electric field and cancels out the stored positive charge. Also, the deposited positive charge can be transported through the IA and evacuated to the irradiated electrode. It is considered that the conductivity of IA is increased [3], and the charge injection barrier of the sample irradiated surface becomes low because of the proton irradiation. These phenomena may be due to changes in the molecular structure, such as the formation of localized levels and the creation of new trap levels. The formation of localized levels is a future issue, as it will require calculations by using molecular orbital methods in future work. The changes in molecular structure is discussed in the next section.

B. XPS measurement

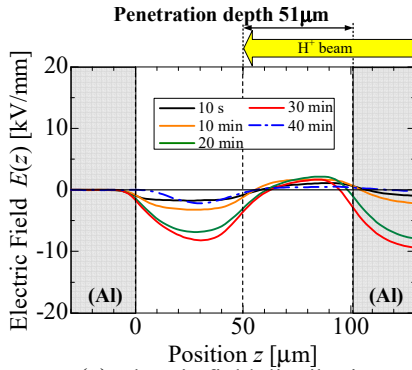
Figure 4 shows the measurement results of the molecular binding energy at C_{1s} on ETFE using XPS. Figures 4 (a) and (b) show the results for the non-irradiated sample and the proton-irradiation sample, respectively. We considered five constituent peaks of the response, C-C, F-C-F, C-O, C-F, and $-\text{CF}_3$. The black, orange, blue, purple, green, and pink lines represent C-C, F-C-F, C-O, C-F, and $-\text{CF}_3$, respectively. The red line means the sum of each constituent peak, which was fitted to the measurement waveform. From Fig. 4, mainly the two peaks at



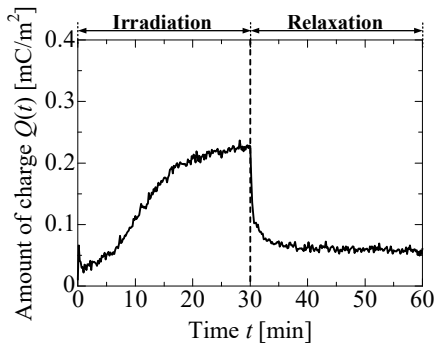
(a) Space charge behavior with time



(b) Space charge distribution



(c) Electric field distribution



(d) Accumulated positive charges in the material with time

Fig. 3. Space charge distribution under proton irradiation

281.9 and 286.8 eV are observed on non-irradiated ETFE, 5 peaks are found on the irradiated ETFE. The result of the non-irradiation sample is consistent with the molecular structure shown in Fig.1. We can see a decrease in the F-C-F peak and an increase in the C-F and C-O peaks. It is the evidence of C-F bonds scission on F-C-F, and oxygen is thought to have bonded to the broken part when the sample is exposed to the air. As for the inside of the sample, oxidation is not revealed. Therefore, broken bonds may remain as radicals, or may have combined with irradiated protons to form ethylene. The increase in ethylene bonds is reported also in the FT-IR results [10]. When radicals are generated, the conductivity of the sample may increase due to the increase in free electrons, which is consistent with the increase in conductivity discussed in the space charge distribution measurement results.

C. NMR measurement

Figure 5 shows the ^1H NMR spectrum of ETFE before and after the proton irradiation. The vertical axis of Fig. 5 shows the measurement intensity. The intensity is standardized to the peak at 2.8 ppm. From Fig. 5 a new peak was observed at 6.9 ppm due to proton irradiation.

Furthermore, we already obtained the NMR spectra on ^{13}C of ETFE [10]. From the result, although CH_2 peak intensity is same between irradiated and non-irradiated sample, the peak becomes broader. And CF_2 intensity peak of irradiated material becomes smaller than in non-irradiated sample.

From the above results, it is suggested that C-F bonds scission occurred on F-C-F and H^+ bonded there. The results are consistent with XPS and FT-IR [10,11] results.

IV. CONCLUSION

In this work, we investigated the relationship between charge accumulation phenomena and modification of molecule structure by proton irradiation using space charge distributions, XPS, and NMR measurement.

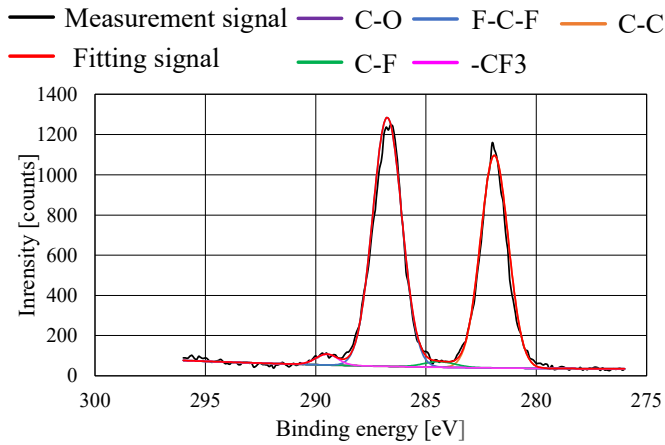
From the measurement results of space charge distribution, positive charges are accumulated during proton irradiation. The position of accumulation of the positive charges was related to the proton penetration depth. However, the injected negative charges from the Al evaporated layer freely transport toward the position of the accumulated proton and compensated for the charges of the accumulated protons. Furthermore, the positive charge accumulation at the NIA was revealed, particularly during the relaxation time. These phenomena were suggested to be caused by a decrease in the charge injection barrier, the formation of new trap levels, and an increase in conductivity. From the results of the modification of the molecular chain using XPS and NMR, we observed C-F bonds scission on F-C-F and the irradiated H^+ replaced F scissored from F-C-F. These phenomena can be considered as one of the reasons for the decrease in the charge injection barrier, the formation of new trap levels, and the increase in conductivity. The formation of localized levels requires more analysis by molecular orbital calculation, which will be further analyzed in future work.

ACKNOWLEDGMENT

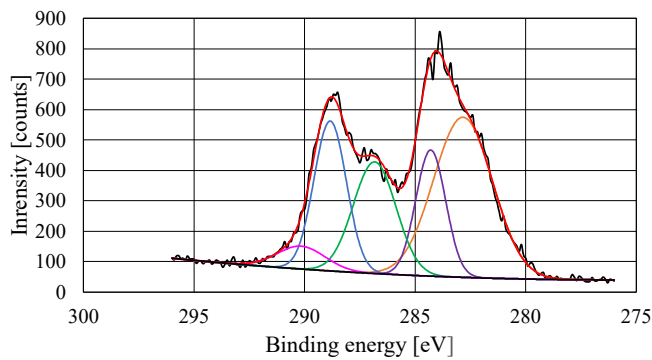
This study was partly supported by the Inter-University Program for the Joint Use of QST (formerly JAEA and JAERI) Facilities and the Shared Use Program of QST Facilities. This work was also supported by JSPS/MEXT KAKENHI Grant Numbers JP18760242, JP23760292, and JP15KK0216. This work was supported by Tokyo City University Nanotechnology Research Center for analysis.

REFERENCES

- [1] A.C. Tribble, "The space environment", Princeton University Press, Chap. 2 and 3, 1995.
- [2] C. Koons, J. E. Mazur, R. S. Selesnick, J. B. Blake, J. F. Fennell, J. L. Roeder and P. C. Anderson, "The impact of the space environment on space systems", Proceedings of the 6th Spacecraft Charging Technology Conference," Air Force Research Laboratory, pp. 7-11, 1998.
- [3] N. W. Green and J.R. Dennison, "Deep dielectric charging of spacecraft polymers by energetic protons", IEEE Trans. Plasma Sci., vol. 36, no.5, pp. 2482-2490, 2008.
- [4] H. Fujii and T. Miyamoto, "Analysis of charged particles environment inside spacecraft affecting internal charging", Proceedings of 53rd Space Sciences and Technology Conference, 1A02, p.5, 2009.
- [5] J. F. Ziegler, J. P. Biersack and U. Littmark, "The stopping and range of ions in solids", Pergamon Press, New York, 1985.
- [6] Y. Li, M. Yasuda and T. Takada, "pulsed electroacoustic method for measurement of charge accumulation in solid dielectrics", IEEE Trans. Dielectr. Electr. Insul., Vol. 1, No. 2, pp.188-195, 1994.
- [7] T. Takada, "Acoustic and optical methods for measuring electric charge distribution in dielectrics", IEEE Trans. Dielectr. Electr. Insul., Vol. 6, No. 5, pp. 519-547, 1999.
- [8] H. Miyake and Y. Tanaka, "Space charge distribution in polymethyl methacrylate and quartz glass irradiated by protons", Sensor and Materials, Vol. 29, No. 8, pp. 1213 – 1222, 2017.
- [9] T. Nagase, T. Mori, H. Miyake and Y. Tanaka, "Space charge accumulation characteristics in ethylene-tetrafluoroethylene copolymer under dc high stress", Proc. IEEE CEIDP, 2015.
- [10] H. Miyake, V. Griseri, U. Chiba, K. Enoki, Y. Tanaka and G. Teysse, "Analysis of charge accumulation phenomena by physicochemical analysis for fluorinated polymer films irradiated by proton", Proc. 15th SCTC, 2018.
- [11] H. Miyake, V. Griseri, T. Mori, Y. Tanaka, G. Teysse and C. Laurent, "Physicochemical analysis for fluorinated polymer films irradiated by proton", Proc. IEEE CEIDP, pp. 106-109, 2017.



(b) Non-irradiation sample



(b) Proton irradiation sample

Fig. 4. Measurement results of the molecular binding energy at C_{1s} on ETFE using XPS

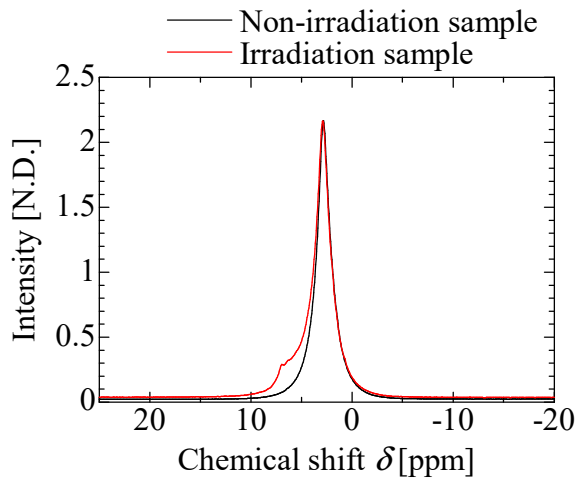


Fig. 5. Measurement results of ¹H on ETFE using NMR