



Title	Electrical Property and Antibacterial Effect of Fly Ash on the Viability of Cariogenic Oral Microorganisms
Author(s)	Yoshino, Katsumi; Take, Hiroyoshi; Kajii, Hirotake et al.
Citation	電気材料技術雑誌. 2000, 9(1), p. 35-40
Version Type	VoR
URL	https://hdl.handle.net/11094/81582
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Electrical Property and Antibacterial Effect of Fly Ash on the Viability of Cariogenic Oral Microorganisms

Katsumi YOSHINO*, Hiroyoshi TAKE* and Hirotake KAJII*

*Department of Electronic Engineering, Graduate School of Engineering,
Osaka University, Yamada-Oka, Suita, Osaka, 565-0871 Japan

Seigo NAGAME** and Takatoshi ONOE***

**Department of Preventive and Community Dentistry, Osaka Dental University

***Department of Microbiology, Osaka Dental University
8-1 Kuzuhahanazono-cho, Hirakata, Osaka, 573-1121 Japan

From viewpoint of recycle of industry waste, the electrical and electrochemical characteristics of pyrolyzed fly ash and their applications have been investigated. Pristine fly ash inherently has a porous structure of carbon and even after high heat treatment, the porosity is maintained. Pyrolyzed fly ash used as the negative electrodes in rechargeable batteries shows good stability and high Coulombic efficiency in charge-discharge cycles in LiClO₄/PC. We demonstrate the possibility to identify the species of oral microorganisms and reduce their activity and colony number by fly ashes.

KEYWORDS : fly ash, battery, Li ion, oral microorganism, antibacterial effect

フライアッシュの電気特性と口腔内細菌への抗菌効果

吉野 勝美、武 弘義、梶井 博武

大阪大学大学院工学研究科電子工学専攻
〒565-0871 大阪府吹田市山田丘2-1

永目 誠吾*、尾上 孝利 **

*大阪歯科大学口腔衛生学講座

**大阪歯科大学細菌学講座

〒573-1121 枚方市楠葉花園町8-1

火力発電所燃焼灰フライアッシュの電子物性及び電気化学的特性とその応用に関して検討を行った。フライアッシュは元々多孔性の構造を有しており、高温焼成後も多孔性を保持している。充放電試験において負極試料として用いられたフライアッシュは安定な充放電電位、極めて高いクーロン率など、優れた二次電池特性を示した。フライアッシュを用いた口腔内細菌の菌種の同定及び抗菌効果の可能性を提案する。

1.Introduction

Carbon materials have been widely used so far for personal and industrial applications such as electrode material for batteries, electrodes for motors, resistors, adsorbent, fibers, fuels, charcoal, painting material, etc. Recently new types of carbon materials such as fullerene C_{60} and carbon nano-tube have been discovered and attracted much attention from both the fundamental and practical viewpoints. We have also proposed new type of periodic porous carbon materials with pores of nano-scale size.

On the other hand, as the waste of power plants utilizing petroleum or coal as fuels, a lot of carbon materials have been formed and considered to be troublesome materials for our environment. Recently we have noticed that such carbons wastes named as fly ash have porous nature of structure and started to study from the fundamental viewpoint. On the other hands, we have explored the effective use of the fly ash for the practical applications¹⁾.

We have also studied electrochemical characteristics of oral cariogenic streptococci and the effect of metals and metal oxides on the streptococci to explore the possibility to identify the species of streptococcus and reduce the number of streptococci^{2~6)}.

In this paper, we discuss on the electrical property of fly ash, characteristics of fly ash as electrode material for the secondary battery and the antibacterial effect of the fly ash on the viability of the several oral microorganisms.

2.Experiment

In this study, the carbon content in pristine fly ash at the thermal power station is about 95%. Pristine fly ash inherently contains some amount of metals such as Ni and Fe that are used as catalysts to accelerate the growth of graphite layers. This fly ash was pyrolyzed at various temperatures for 1 h in a high-purity Ar atmosphere. The samples for electronic measurement were pressed into a sheet at $400\text{kgf} \cdot \text{cm}^{-2}$. The electrical conductivity and its temperature dependence were measured by a conventional four-probe technique using a Quantum Design PPMS. Electron microscope images of the morphology of pristine and pyrolyzed fly ashes were obtained by a scanning electron microscope (SEM) (S-2100A, Hitachi).

For preparation of a pellet - type electrode, fly ashes were mixed with 10wt% Teflon powder and pressed on a Ni mesh at $100\text{kgf} \cdot \text{cm}^{-2}$. A Lithium metal plate served as the counter and reference electrodes. The electrolytes used in this study were a 1M or 2M solution of LiClO_4 in a propylene carbonate (PC) in the case of pyrolyzed fly ashes with the HTTs of below 1400°C and a 1M solution of LiPF_6 in a 7 : 3 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) by volume in the case of pyrolyzed fly ashes with an HTT of 2800°C . Electrochemical measurements, including charge-discharge test were carried out using a beaker-type cell at room temperature in an argon-filled glove box (Miwa, MDB-1-B+MS80).

In this study, microorganisms such as *Actinomyces viscosus* (*A.v*), *Streptococcus faceium* (*S.f*), *Streptococcus mitis* (*S.m*), *Streptococcus sanguis* (*S.s*), *Lactobacillus acidophilus* (*L.a*) and *Lactobacillus casei* (*L.c*) were used. For the pre-cultivation of these resident floras, Trypticase soy broth (TSB; Becton Disk-

inson and Co., Cockeysville, MD, U.S.A.) was used. After 48 hr, the cultured medium which was in the logarithmic phase was diluted and centrifuged. The precipitated microorganisms were washed with a small amount of phosphorus buffer and recentrifuged. These obtained microorganisms were dispersed in a neutral phosphorus buffer solution (pH7). Concentration of each microorganism in the above solution containing fly ash (concentration ratio: 0.1%) was 1×10^5 CFU (colony forming unit)/ml. Cultivation of the suspensions in an aerobic growth chamber, at 37°C, 55% relative humidity. Samples of the treated suspensions were incubated on TS agar plates. After 48 hr of cultivation at 37°C, the number of viability cells was counted.

3. Results and discussion

3-1 Electrical property of fly ash

Figure 1 indicates the scanning electron microscope images of the pristine and pyrolyzed fly ashes. As evident in this figure, fly ash contains many small pores of micro- and nano- scales in diameters. Even after a heat treatment at 2600°C, pyrolyzed fly ash maintains porosity and the surface of the pyrolyzed fly ash is more smooth than that of pristine fly ash.

The normalized temperature dependence of resistivity $\rho_r(T) = \rho(T) / \rho(200K)$ in pristine and pyrolyzed fly ashes is presented in Fig.2. The resistivity of the fly ash does not exponentially decrease with temperature. In the critical region of metal-insulator transition, the temperature dependence of resistivity obeys the power law dependence as given by

$$\rho(T) \propto T^{-\beta} \quad (1)$$

, where β lies within the range $1/3 < \beta < 1$ ⁷⁾. These β values of the pristine fly ash and pyrolyzed fly ashes

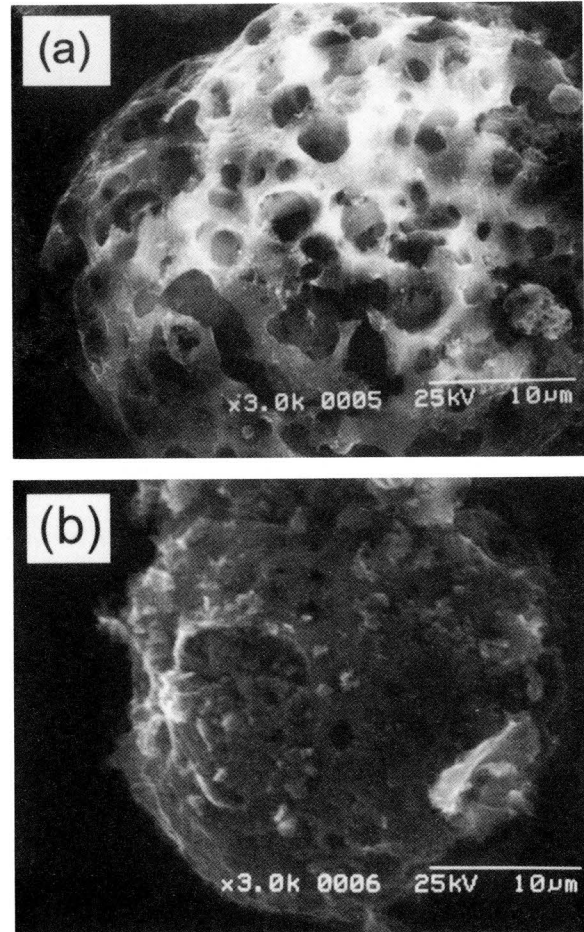


Fig.1: Scanning electron microscope images of (a) a pristine fly ash and (b) a pyrolyzed fly ash with a heat treatment temperature (HTT) of 2600°C.

with the heat treatment temperatures (HTTs) of 1400 and 2600°C were evaluated from the slope of the straight lines in the Fig.2 to be 0.32, 0.17 and 0.17, respectively. In general, the conduction process is metallic if $\beta < 1/3$. The conduction process between particles of the fly ash becomes more metallic with increasing the HTT.

3-2 Characteristics of fly ash as electrode material of secondary battery

From the viewpoint of the recycle of industry waste, we have also investigated the electrochemical properties of a pristine fly ash and pyrolyzed fly ashes with various HTTs as negative electrode materials of a lithium ion secondary battery. Figure 3 shows the third

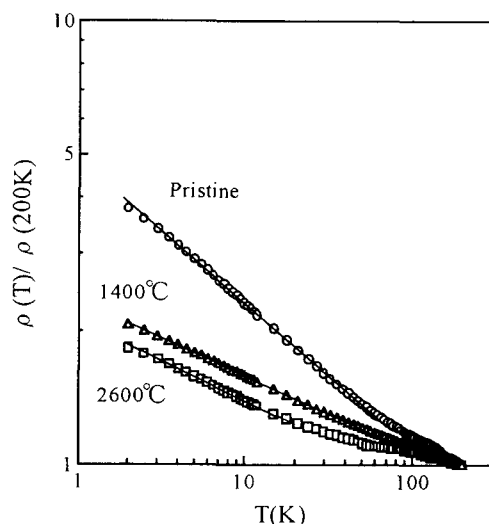


Fig.2: Normalized temperature dependence of resistivity $\rho(T) = \rho(T)/\rho(200\text{ K})$ in a pristine fly ash and pyrolyzed fly ashes with the HTTs of 1400 and 2600°C.

charge-discharge profiles of the pristine fly ash and the pyrolyzed fly ashes with HTTs of 1100, 1400 and 2800°C. The charge-discharge test was employed under the constant current corresponding to 20mA/g. The discharge capacity of pyrolyzed fly ash with an HTT of 1100°C is the highest. That is, the charge-discharge characteristic of fly ash can be improved by pyrolysis. The discharge capacities of the pristine fly ash and the pyrolyzed fly ashes with the HTT of 1100, 1400 and 2800°C were about 156, 223, 168 and 161 mAh/g, respectively. In all cases, the Coulombic efficiency is more than 90 %. As graphitization progresses, the curve of the pyrolyzed fly ash with the HTT of 2800°C is flattest in the region of about 0V vs the Li electrode, as is generally known for well-ordered graphite.

3-3 Antibacterial effect of fly ash on the viability of the various oral microorganisms

Figures 4, 5 and 6 show the change in the viability of the oral microorganisms such as *A.v*, *S.f*, *S.m*, *S.s*, *L.a* and *L.c* with the fly ashes. As evident in Fig.4, the number of viability cells of *A.v* decreases with increasing time. In the case of the oral microorganisms

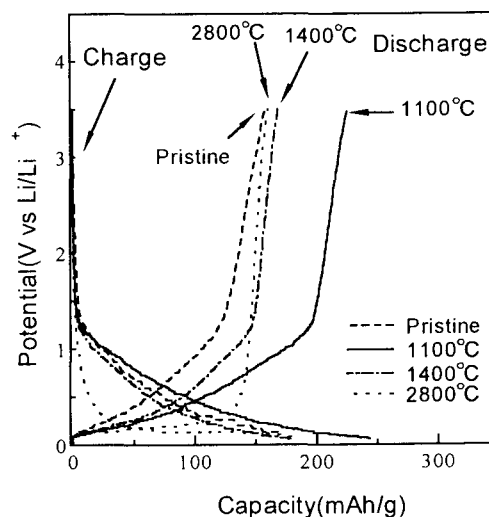


Fig.3: Charge-discharge profiles at the third cycle for pristine and pyrolyzed fly ashes with the HTTs of 1100, 1400 and 2800°C. The charge-discharge test was employed under the constant current corresponding to 20mA/g.

such as *S.m* and *S.s* as shown in Fig. 5, the number of viability cells markedly decreases with increasing time. While, the number of viability cell of *S.f* does not drastically decrease. Especially, in the case of *L.a*, the number of viability cells is maintained after 3 hours. It should be noted that except for *L.a*, the livability of all other oral microorganisms such as *A.v*, *S.f*, *S.m*, *S.s* and *L.c* decreases with increasing time.

These results clearly indicate that the fly ash is effective for reducing the density and activity of oral microorganisms. It should also be mentioned that the selectivity of the species of oral microorganisms exists in the effect of fly ash.

The activity of oral microorganisms seems to be confined in micro pores of fly ash, resulting in the suppression of the growth of oral microorganisms. It is not clear whether the oral microorganism is completely killed or just the growth is hindered at this stage.

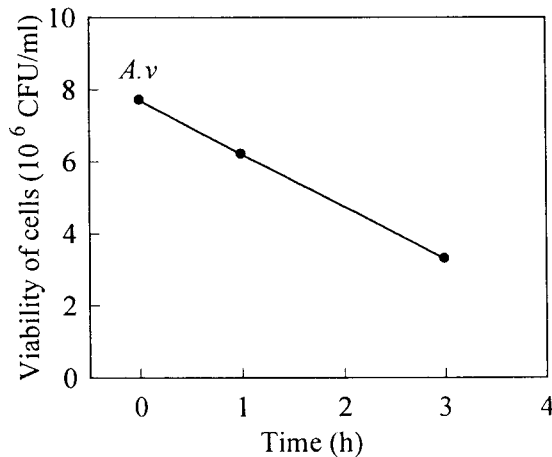


Fig.4: The change in the viability of *Actinomyces viscosus* (*A.v*) with the fly ash.

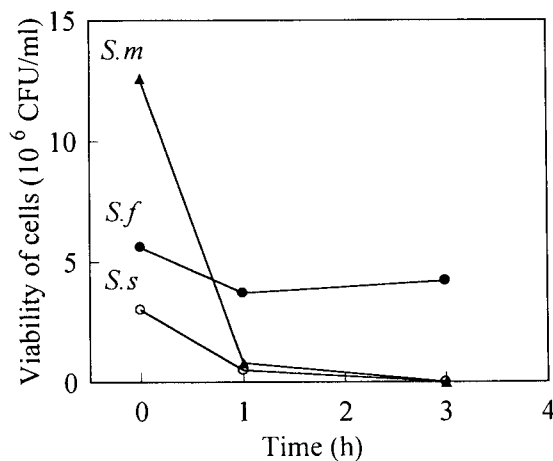


Fig.5: The change in the viability of oral microorganisms such as *Streptococcus faceium* (*S.f*), *Streptococcus mitis* (*S.m*) and *Streptococcus sanguis* (*S.s*) with the fly ash.

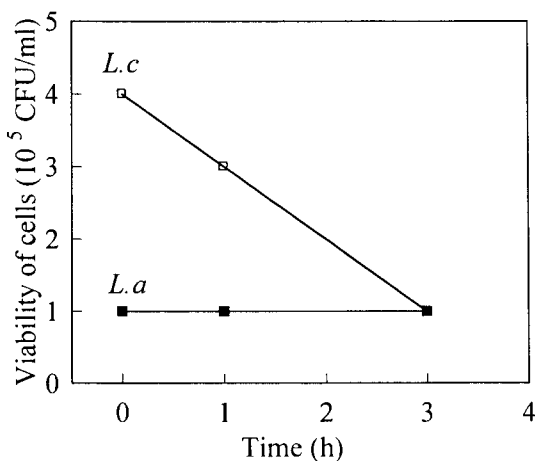


Fig.6: The change in the viability of oral microorganisms such as *Lactobacillus acidophilus* (*L.a*) and *Lactobacillus casei* (*L.c*) with the fly ash.

4. Conclusion

Pristine and pyrolyzed fly ashes contain many small pores of micro- and nano- scale sizes in diameters. The electrodes of pyrolyzed fly ash showed good stability and high Coulombic efficiencies in charge-discharge cycles in LiClO_4/PC . From the viewpoints of recycle of industry waste, we propose to apply the fly ash to a negative electrode of lithium ion secondary battery. We demonstrate the possibility to identify the species of oral microorganisms and reduce the number of those by using fly ashes.

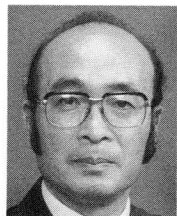
Acknowledgements

Part of this study was carried out as Cooperative Research of Creation and Education of Novel Characteristics of Nano-size Molecular System supported by Fund of Research for the Future of the Japan Society for the Promotion of Science (Project No. JSPS-RFTF96P00206). The authors wish to thank Dr. Eriko Yagasaki (The Kansai Electric Power Company) for the sample and support.

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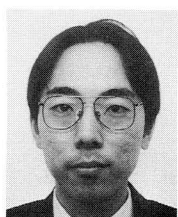
(1999年1月31日受理)



Katsumi Yoshino was born in Shimane on December 10, 1941. He graduated in 1964 from Department of Electrical Engineering, Faculty of Engineering, Osaka University, where he obtained a Doctor of Engineering Degree in 1969. In that year, he became a Research Associate in Electrical Engineering, Osaka University. He was promoted to Assistant Professor in 1972 and Associate Professor in 1978. In 1988, he became a Professor in Electronic Engineering. He has been engaged in research on organic functional materials such as conducting polymers. He received an Applied Physics Society Award, Osaka Scientific Award, Book of Year Award and Outstanding Achievement Award from the Institute of Electrical Engineers of Japan in 1981, 1990, 1997 and 1998, respectively. He authored or co-authored more than 32 books. He is a member of the Institute of Electrical Engineers in Japan, Japan Physical Society, Applied Physical Society, and Polymer Society.



Hiroyoshi Take graduated from Department of Electronic Engineering, Osaka University in 1999. He is now Master course student of Department of Electronic Engineering, Graduate School of Engineering, Osaka University and now studying the electronic and optical properties of carbon materials and application of them to electronic devices such as batteries. He is a member of the Japan Society of Applied Physics.



Hirotake Kajii received B.S., M.S. and Ph.D. degrees in Electronic Engineering from Faculty of Engineering, Osaka University, Japan in 1996, 1998 and 2000, respectively. In 2000, he joined the Collaborative Research Center of Applied Science and Technology, Osaka University, where he is currently a research associate. His research interests are in the electronic and optical properties of carbon materials and dyes, and application of them to electronic devices such as batteries, FED, photocell and LED. He is a member of the Institute of Electrical Engineers of Japan and the Japan Society of Applied Physics.



Seigo Nagame was born on 1949. He graduated in 1974 from Osaka Dental University. He has obtained his degree of Doctor of Dentistry from Osaka Dental University. In 1974, he became a Assistant in Department of Preventive Dentistry, Osaka Dental University. He was promoted to Instructor in 1980. In 1995, he became a Associate Professor in Department of Preventive and Community Dentistry, Osaka Dental University. He has been engaged in research on antibacterial effects of the powdered semiconductor titanium oxide with photocatalytic reaction and dental caries prevention. He is a member of Japan Dental Society, Japanese Society for Dental Health, International Association for Dental Research, Japanese Society of Public Health, Japanese Society of Periodontology, and Japanese Society of Pediatric Dentistry.



Takatoshi Onoe was born on 1943. He graduated in 1971 from Graduate School of Agriculture, Kagawa University. He has his degree of Doctor of Agriculture from Nagoya University. In 1975, he became a Assistant in Department of Bacteriology, Osaka Dental University. In 1985, he became a Lecture in Department of Bacteriology, Osaka Dental University. He has been engaged in research on susceptibility of oral bacteria to chemotherapeutics and other substances, the β -lactam antibiotics resistant mechanisms of oral anaerobic gram negative rods, ultrastructural observation of the surface structure of cariogenic and periodontopathic bacteria and cytological studies on the mechanism of resistance expression in the Crown rust disease of oat. He is a member of Japanese Society of Bacteriology, Japanese Society of Chemotherapy, Japanese Society of Electron Microscopy, Japanese Society of Electron Microscopy Technology for Medicine and Biology, Japanese Association for Oral Biology, International Association for Dental Research and Phytopathological Society of Japan.