

T I C

TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

PRESIDENT'S LETTER

Dear friends and fellow T.I.C. members,

I hope this note finds you all well. In the northern hemisphere, spring has finally arrived erasing the memory of some very severe weather this winter. Meanwhile, fall is taking hold in the southern hemisphere hopefully also erasing the memories and impact of some very severe summer weather.

Your Executive Committee met in Brussels on Monday April 7th for its biannual meeting. We had a very full agenda with many interesting and concerning topics. One topic of particular concern and importance to all members was the resurgence of thefts of tantalum raw materials out of Dar es Salaam. Fresh in our minds is the negative impact the last instance of thefts from this port had on one company's membership of the T.I.C. This should act as a clear reminder that these materials will appear for purchase somewhere in the world and that as members committed to the T.I.C. Artisanal and Small Scale Mining Policy we have a duty and obligation, not only to each other but to the global community, to perform the necessary due diligence on the provenance of 'conflict' minerals and all minerals in general. The T.I.C. as a body has proven that it takes this matter seriously and that, to the extent possible, it will use the membership status in the association as a lever in sending a clear message to the membership and the global community that it takes a strong leadership position on this matter. No one should be caught unaware of this Policy and the potential impact on T.I.C. membership. In addition to the impact on membership, we communicate all such decisions and findings to the EICC/GeSi board. Be warned and be aware.

At this Executive Committee meeting we also had a session with representatives of King-Tan Tantalum Industry whereby they were able to address the issue of their suspension and answer questions from the Committee. We have an agreement with King-Tan regarding what we, as your Executive Committee, see as the necessary steps towards reinstatement to active member status. We will report on this status at the Fifty-fifth General Assembly in New York City in October.

Speaking of the General Assembly in New York City, plans are well on their way to make this another memorable meeting. We would like to thank in advance Hi-Temp Specialty Metals for welcoming us to visit their plant in Yaphank, on Long Island. The Executive Committee reviewed a number of abstracts for technical papers and we are looking for a few more in specific areas of niobium and downstream processing in order to have a necessary and representative balance. Committee members are reaching out now to member companies in order to finalise the technical programme. In addition to the technical papers we will also have a few papers on the status of governmental policies on critical raw materials as well as the status of conflict minerals policy and field activity.

This year we will be using an online process for hotel reservations for the General Assembly. Please make certain you make your reservations early in order to get the T.I.C. meeting discount. Once the reservation period is closed (on September 19th) we will no longer have any way of gaining this special rate or guaranteeing rooms at the venue. Also, if you require a visa to visit the US, I cannot stress enough the need to get this process completed as soon as possible. We had no-shows in York last year as some delegates waited too long to obtain their visas and were not able to join the meeting.

Well that is it for now. I wish you and yours health and prosperity and look forward to any and all communications regarding issues relevant to the T.I.C. and membership as a whole.

Regards,

Dr Daniel F. Persico (Dan)
President

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FIFTY-FIFTH GENERAL ASSEMBLY

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The Fifty-fifth General Assembly and associated technical meeting of the Tantalum-Niobium International Study Center will be held in New York City, U.S.A., from Sunday October 12th to Wednesday October 15th 2014. The conference will take place at the Sheraton New York Times Square Hotel, where a block booking of bedrooms has also been secured.

The administration of the association will be carried out in the formal General Assembly on the morning of Monday October 13th, including election of applicants for membership of the association and the appointment of the members of the Executive Committee.

Technical presentations will follow, extending until early afternoon on Monday and Tuesday. On Wednesday October 15th, a plant tour will be organised to visit the facility of Hi-Temp Specialty Metals in Yaphank, on Long Island.

A social programme is also being prepared, including a welcome reception on Sunday October 12th and a gala dinner on the evening of Monday October 13th. We are also organising sightseeing tours for those accompanying delegates, to discover the bustling city of New York and its surroundings.

An invitation will be sent to the nominated delegate of each member company in July. Non-members who would like to attend should contact the T.I.C.

METAL DUSTS AND CERTAIN CONSIDERATIONS WHEN DEFINING A SUITABLE BASIS OF SAFETY

Paper presented on October 14th 2013, as part of the Fifty-fourth General Assembly of the T.I.C., held in York, England. Paper written by Michael Merritt and David Firth from Chilworth Technology Ltd (a DEKRA company) and presented by Nigel Allen.

INTRODUCTION

Generating a dust cloud explosion is relatively easy, but in practice prevention of an explosion is often more difficult to achieve. When handling metal powders with high ignition sensitivity, strong explosion characteristics and a propensity to form dust clouds during normal processing conditions, it is vital that manufacturers and processors understand the need to control ignition risks and mitigate explosion effects. The risks of explosion can be further exacerbated through the liberation of highly flammable gases such as hydrogen when in contact with water, and in these circumstances good process risk control becomes even more important to safe operation of the process. The measures taken to reduce fire and explosion risks are known as the Basis of Safety and are supported by a stringent testing programme to define a safe operating envelope for the process.

INCIDENTS

Industrial fires and explosions have been a hazard for as long as man has been processing, storing and transporting materials. There are countless case studies of incidents which have involved the more common organic based materials. However, due to increased demand from industries such as automotive and aviation there have also been several devastating explosions and fires involving metal dusts in recent times. The fear is that if production increases further so will the frequency of incidents.

One example of metal dust incidents are the metal dust flash fires that occurred at the Hoeganaes Corporation facility in Gallatin, Tennessee, U.S.A. in 2011, which resulted in a number of injuries and fatalities. Prior to the incidents the facility had increased its manufacturing capability by over 500% since the 1980s. The first incident involved a bucket elevator which apparently became misaligned, resulting in increased torque on the motor which subsequently shut down. On inspection, the maintenance staff was confident that the elevator was not misaligned and gave the order to restart the motor. The resultant vibration dislodged iron dust which had been allowed to accumulate over time. A large flammable dust cloud was formed which subsequently ignited. A second incident occurred only a few months following this, when dust accumulations on surfaces were dislodged and a secondary dust explosion occurred. After a further few months a third incident involved hydrogen gas used to reduce the iron powder. This incident resulted in three fatalities and two injuries.

The findings of the ensuing US Chemical Safety Board (CSB) investigation found that one cause of the second incident was poor housekeeping which led to dust accumulations on ledges and in surrounding areas. In the case of the third hydrogen incident, the initial hydrogen explosion was enough to dislodge the dust and form secondary flammable atmospheres. It was this occurrence that had the devastating effect and which led to the fatalities.

An undesirable characteristic associated with metal dusts is that when they combust they burn hotter and often for longer than organic materials. The burning dust also adheres very well to clothes and skin. Clothes then melt or ignite as a result of the intense heat, so skin burns tend to be more severe and life threatening.

DATA ON FLAMMABILITY / EXPLOSION SEVERITY

There is a large amount of published data relating to the flammability of metal dusts, such as the BIA publication [1]. Despite the information specifying particle size data, much care must be exercised when using the BIA and other data and it should not be directly used in the definition of a Basis of Safety without supporting evidence that it genuinely relates to the product being assessed. Even minor differences between batches of the same material can yield different flammability test data. An example of this is the effect of particle size for some metal dusts. Very small (micronized) particles of aluminium and magnesium dust have high sensitivity to ignition from electrostatic sparks i.e. a low capacitive Minimum Ignition Energy (MIE). However, increasing the particle size will increase the dust MIE. Some values reported in the BIA reference state MIEs > 1 J for the same material. What is more, particle shape will also have a direct influence on flammability parameters. A particle with a large surface area will tend to burn longer and more vigorously compared to the same material with less surface area.

The explosion severity characteristics of metal dusts can also vary greatly. Again, factors such as particle size, moisture, level of oxidation on the particulate surface and particle shape (surface area) will have a direct effect on the measured explosion severity of the dusts. Chilworth Technology's laboratories in Southampton have tested a number of metal dusts; and while some fine aluminium and magnesium powders exhibit peak pressures more than 12 bar g with rates of pressure rise greater than 1500 bar.s⁻¹, other dusts were seen to exhibit only moderate peak pressures of 7 bar g and rates of pressure rise at around 500 bar.s⁻¹. Clearly, other factors were at play here but the point is that care must be taken when using published data. It is always better to have your own product tested to define the explosion risk parameters.

EXPLOSION PROTECTION TECHNIQUES

Explosion venting is a popular explosion protection technique used in the processing industries to protect enclosures from the effects of internal explosions. The methodology is described in a number of national and international published standards such as BSEN 14491 [2] and NFPA 68 [3] is based upon tests performed by various research establishments and explosion protective device manufacturers. However, very few examples of metal dust venting tests have been published, so the question raised is 'Can these same principles be applied for metal dust explosions?'

Recent experimental studies [4] investigating the applicability of the methodology described in literature for metal dust explosions showed that for aluminium dust the vessel reduced overpressures after explosion were seen to be higher than predicted by the venting equations. The reduced overpressure is the residual pressure seen within a vessel fitted with an explosion vent that has successfully opened. This suggests that, owing to the unique combustion properties of some metal dusts, there is a need to use specific vent sizing methods rather than apply the standard methodology.

Explosion suppression is another explosion protection technique. This is the process of controlling explosions by rapidly injecting a material that either chemically quenches the combustion reaction (e.g. halon) or absorbs the energy produced. Some act by terminating chain branching reactions such as halon whilst others absorb the thermal and radiant energies created by the combustion reaction such that the fuel particles cannot sustain combustion and the reaction propagation is prevented.

The results of recent test studies [4] investigating the effectiveness of suppression systems on metal dust explosions showed that, although most suppression systems are effective in protecting enclosures from the effects of metal dust explosions, the use of multiple, smaller canisters to discharge the inert medium coupled with ultra-fast pressure detectors is more effective than the standard approach. This demonstrates again that the direct application of 'tried and tested' measures for organic flammable dusts is not always acceptable for metal dusts and that every scenario should be examined on a case by case basis.

EXPLOSION ISOLATION

Explosion isolation devices such as fast acting mechanical valves and chemical barriers are used to prevent pressure and flames associated with a dust explosion from being passed from the point of ignition into interconnected equipment. There is ample experimental evidence to show that flame speed and pressure increase as the explosion propagates through pipelines. Turbulence generated at the walls of pipelines and obstructions such as bends exacerbate the situation resulting in an increase in the combustion rate and hence flame velocity leading to the potential for explosion transition from deflagration (sub-sonic speed) to detonation (super-sonic speed).

Again, there is little experimental evidence which supports the effectiveness of isolation devices with metal dusts that possess high explosion severity characteristics (i.e. powder K_{st} values > 650 m bars⁻¹). When metal dusts are seen to exhibit severe explosion severity characteristics and there is a requirement to fit explosion isolation in an elongated length of duct or pipe there is the need to fit supplementary explosion relief panels to moderate the explosion pressure within the line and prevent the transition from deflagration to detonation.

OTHER AREAS OF POTENTIAL RISK

Dusts of most metals, alloys, carbides, hydrides and nitrides can exhibit pyrophoric behaviour. Pyrophoricity is the rapid oxidation of the dust on exposure to air and tends to occur when the particle size of the dust is very small (i.e. < 1 micron). The resultant exothermic reaction usually results in combustion of the material which could easily be a potential ignition source for a primary or secondary explosion.

Furthermore, many metal dusts will react in contact with water, acids and/or bases and liberate flammable gases such as hydrogen. For example, aluminium is well known for liberating hydrogen gas when in contact with water. This undesirable characteristic causes issues with regards to fire fighting methods. The potential for flammable gas generation will also further complicate the formulation of a robust Basis of Safety.

CONCLUSION

The subjects touched on in this paper are only a small sample of the problems encountered when defining a Basis of Safety for some metal dusts. Adopting the same approach as for flammable organic solids could lead to a situation where a flawed Basis of Safety is determined. The best way to design robust mitigation measures is by assessing each operation for each material on a case by case basis. It is therefore strongly recommended that expert help be sought.

REFERENCES

1. BIA Report 13/97, Combustion and Explosion Characteristics of Dusts, HVBG.
2. BS EN14491 (2012), Dust Explosion Venting Protective Systems, BSI.
3. NFPA 68, Standard on Explosion Protection by Deflagration Venting, 2013 edition. National Fire Protection Association.
4. Explosion Protection with Metal Dust Fuels: New Experimental Evidence. Taveau J.R., Vingerhoets J., Snoeys J., Going J.E. and Farrell T.M. Fike Corporation, Industrial Protection Group.

THE EFFECT OF ADDITIVES TO THE CONDUCTIVE POLYMER SOLUTION FOR LOW-ESR ELECTROLYTIC CAPACITORS

Paper presented on October 14th 2013, as part of the Fifty-fourth General Assembly of the T.I.C., held in York, England. Paper written by Yasuhiro Tomioka, Yasuhisa Sugawara and Koji Sakata from NEC TOKIN Corporation and presented by Takashi Kono.

INTRODUCTION

There is a growing need for low-ESR (equivalent series resistance) electrolytic capacitors which can be used as coupling and/or bypass capacitors. A high-conductivity electrolyte is required for such a low-ESR electrolytic capacitor, because the ESR of an electrolytic capacitor mainly depends on the electrical conductivity of its electrolyte. Conventionally, manganese dioxide has been used for tantalum capacitors and an electrolytic solution or a TCNQ complex for aluminum capacitors. However, their conductivity is at most 10 S/cm (see Table 1).

Recent studies led to the development of conductive polymers having a conductivity as high as at least 10 S/cm, which are now being used as an alternative electrolyte and successfully providing low-ESR electrolytic capacitors.

Figure 1 shows the ESR-frequency characteristics of electrolytic capacitors that are based on different electrolytes. NeoCapacitor, a tantalum capacitor which is based on a conductive polymer as its electrolyte, has a low ESR and excellent frequency characteristics, compared to the electrolytic capacitors of other electrolytes.

Although the use of conductive polymers has brought low-ESR electrolytic capacitors, the present industrial situation demands smaller and smaller electrolytic capacitors with a further lowered ESR. Therefore it is necessary to develop a technology to lower the ESR of electrolytic capacitors. In this study we developed a method to increase the conductivity of conductive polymers, whereby the ESR of electrolytic capacitors can be further lowered. Specifically, we added additives to a conductive polymer solution and analyzed the effect of the additives to increase the conductivity of the polymer and to lower the ESR of the corresponding solid electrolytic tantalum capacitor. In addition, the recent demand for electrolytic capacitors with higher reliability prompted us to perform reliability testing of these low-ESR, solid electrolytic tantalum capacitors.

Finally, we analyzed the mechanism of the additives to improve the conductivity of the conductive polymer film and to lower the ESR and increase the reliability of the solid electrolytic tantalum capacitor.

| Conductivity (S/cm) | Electrolyte |
|---------------------|---------------------|
| 10~ | Conductive Polymer |
| 1~10 | TCNQ |
| 1~0.1 | MnO ₂ |
| 0.1 | Electrolytic Liquid |

Table 1: Conductivity of electrolytes for electrolytic capacitors

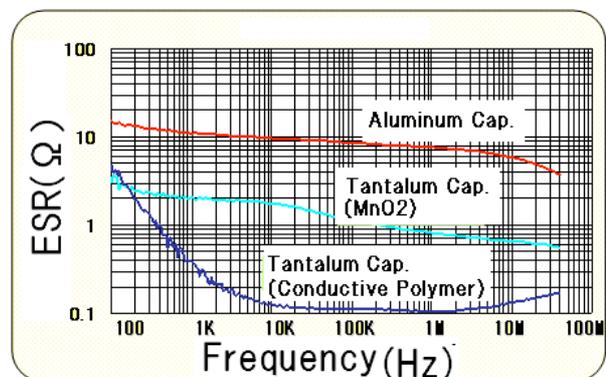


Figure 1: ESR-frequency characteristics of capacitors

CONDUCTIVE POLYMERS

After being discovered in 1976 by Dr Hideki Shirakawa (Prof. Emeritus, University of Tsukuba), various conductive polymers have been developed, e.g. the synthesis of PEDOT in the 1980s by Bayer AG. To obtain conductive polymers, chemical doping with dopant molecules (e.g. halogen) or electrochemical doping is used to afford high conductivity to conjugated polymer molecules (e.g. polyacetylene). In other words, synthesis of a conductive polymer requires (i) polymerization of conjugated polymer molecules and (ii) charge injection into the conjugated polymer through doping.

In order to form a conductive polymer layer on an electrolytic capacitor, any of the following methods is commonly used:

- (1) The electrolytic capacitor is successively immersed in a solution containing the monomers for the conductive polymer and an oxidant and a dopant solution, so that the conductive polymer is directly polymerized on the electrolytic capacitor ('in situ polymerization').
- (2) An electric current is passed through the electrolytic capacitor in an electrolytic solution containing the monomers and a dopant, for electrochemical polymerization and doping to occur ('electrolytic polymerization').
- (3) After a solution of the conductive polymer is prepared and applied to the electrolytic capacitor, it is dried to form the conductive polymer layer.

The method based on a conductive polymer solution (3) allows the conductive polymer layer to be easily prepared, and it is thus suited for stable mass production. Accordingly, industrial material manufacturers are striving to develop better conductive polymer solutions.

CONDUCTIVE POLYMER SOLUTIONS

Polyanilines, polypyrroles and polythiophenes are commonly used polymers for conductive polymer solutions. The polyanilines can alter their properties in response to their oxidation state, the polypyrroles are inexpensive, and the polythiophenes are stable against external (environmental) perturbations. Among these, the polythiophenes are often used because of their stability against external (environmental) perturbations. The use of polythiophene conductive polymers has been steadily increasing, accounting for about 70% of the conductive polymer market in FY 2008.

PEDOT:PSS is the most commonly used of the existing polythiophene conductive polymer solutions (see Figure 2). PSS is a dopant to increase the conductivity of the polymer, but also improves the dispersion into water as well as the film formation. PEDOT:PSS can stay stably dispersed in an aqueous solution and it can be dried to form a conductive polymer film with a high conductivity and excellent film properties.

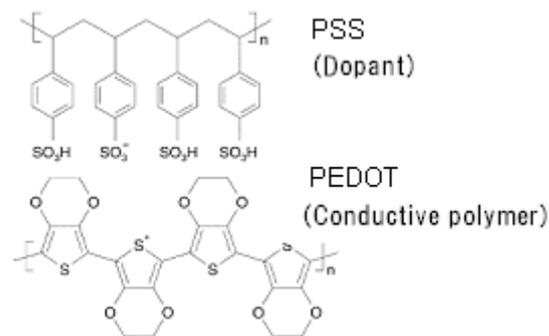


Figure 2: Structure of PEDOT and PSS¹

DEVELOPMENT OF IMPROVED HIGH-CONDUCTIVITY POLYMER

Addition of an additive to a conductive polymer solution is known to improve the conductivity of the corresponding conductive polymer film, made of the conductive polymer solution. One example is the addition of ethylene glycol to a PEDOT:PSS conductive polymer solution. In this case, the additive (i) improves the crystallization in the conductive polymer particles in the resulting film to increase the electron mobility between the conductive polymers and (ii) makes the PEDOT/PSS ratio more uniform across the film to increase the electron mobility between the conductive polymer particles, as revealed by XRD and XPS.

In addition, it has been reported that the addition of ethylene glycol to a PEDOT:PSS solution can provide an aluminum electrolytic capacitor with lower ESR^{1, 2}.

Based on the previous findings, we chose to add additives to a conductive polymer solution in order to increase the conductivity of the resulting conductive polymer film and to lower the ESR of the corresponding solid electrolytic tantalum capacitor. The reliability of the improved solid electrolytic tantalum capacitors was also tested.

Finally, the mechanisms of the improved conductivity of the conductive polymer films and the lowered ESR and the increased reliability of the solid electrolytic tantalum capacitors were investigated.

A conductive polymer has three types of conductive paths: (i) a conductive path in the single conductive polymer, (ii) a conductive path between the conductive polymer chains, and (iii) a conductive path between the conductive polymer particles (see Figure 3). Increasing the conductivity of any path can result in a conductive polymer film with improved conductivity.

In the present study, addition of additives to a conductive polymer solution improved the conductivity of the resulting conductive polymer film. The mechanism of the improved conductivity was examined in

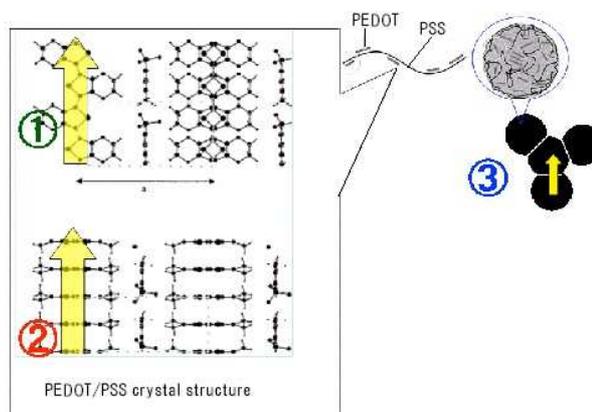


Figure 3: Conductive paths of a conductive polymer

terms of the three conductive paths as described above. The lowered ESR and the increased reliability of the improved solid electrolytic tantalum capacitors were analyzed in terms of film properties, i.e. the distribution of the film constituents and the chemical bonds in the conductive polymer film.

METHODS

PREPARATION OF CONDUCTIVE POLYMER SOLUTIONS, FILMS, AND SOLID ELECTROLYTIC TANTALUM CAPACITORS

Table 2 shows the additives used in the test samples of this study. In order to prepare the test samples, the additives were mixed with separate PEDOT:PSS dispersions. The obtained conductive polymer solutions were applied to separate glass slides and dried to form test conductive polymer films.

The conductive polymer solutions with or without either additive were also used to prepare electrolytes for preparing solid electrolytic tantalum capacitors. In order to prepare any of the capacitors, a tantalum pellet was provided with a dielectric layer by chemical processing. Then a conductive polymer layer was formed on the pellet by in situ polymerization. The pellet was immersed in one of the conductive polymer solutions, taken out of the solution, and dried to form a conductive polymer film on the conductive polymer layer by in situ polymerization. Then Gr (graphite) and Ag layers were formed thereon.

| Level | Contents |
|-------------|-----------------------|
| No additive | PEDOT/PSS |
| Additive A | PEDOT/PSS+ Additive A |
| Additive B | PEDOT/PSS+ Additive B |

Table 2: Additives used in the test samples

EVALUATION/ANALYSIS OF CONDUCTIVE POLYMER FILMS AND SOLID ELECTROLYTIC TANTALUM CAPACITORS

The effect of the additives on the conductivity of the conductive polymer films was evaluated by surface resistance measurement. The ESR of the obtained solid electrolytic tantalum capacitors was determined at 100 kHz using an LCR (inductance, capacitance and resistance) meter. The solid electrolytic tantalum capacitors were also subjected to a reliability test (ESR at 125 and 65 degrees Celsius, 95% RH, 100 kHz).

Table 3 is a list of the methods used to analyze the test conductive polymer films. For each of the conductive polymer films, the effect of the additives on the conductivity was analyzed by XRD (X'Pert-MPD, PANalytical) and XPS (Quantum 2000, ULVAC-PHI). Their film properties were studied by FT-IR (Spectrum One/AutoIMAGE, PerkinElmer).

| Method | Analysis matter | Purpose |
|--------------------|-----------------------------------------|-------------------------------------|
| Surface resistance | Electrical conductivity of coating film | Original Electrical conductivity |
| XRD | Crystallization of PEDOT | Path② (Between molecular chains) |
| XPS | PEDOT/PSS ratio dependence of Depth | Path③ (Between particles) |
| FT-IR | Chemical bonding in coating film | Chemical bond by Additive |

Table 3: List of methods used to analyze the test conductive polymer films

In the surface resistance measurement, a four-probe method (Loresta-GP, Mitsubishi Chemical Analytech) was used to determine the surface resistance. The conductivity of the conductive polymer films was calculated according to their thickness. In order to determine the PEDOT/PSS ratio at various detection depths by XPS, the photoelectron take-off angle was appropriately adjusted to give a desired photoelectron detection depth from the film surface (see Figure 4).

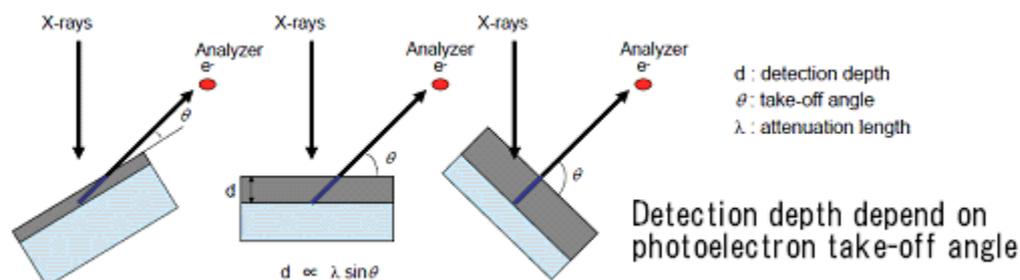


Figure 4: Relationship between the photoelectron take-off angle and the detection depth in XPS

RESULTS AND DISCUSSION

THE EFFECT OF ADDITIVES ON THE CONDUCTIVITY OF A CONDUCTIVE POLYMER FILM

Table 4 shows the surface resistance, thickness and conductivity of the test conductive polymer films prepared for this study.

When no additive was added to the polymer solution, the surface resistance of the conductive polymer film was as high as 9391 Ω /sq. In the films each made from a polymer solution containing an additive ('additive A' and 'additive B'), the surface resistance became much lower (189 Ω /sq and 172 Ω /sq respectively). The film thickness differed only slightly between the 'no additive' film (2.7 μ m) and the 'additive A' and 'additive B' films (3.0 μ m and 3.3 μ m respectively). Accordingly, each of the 'additive A' and 'additive B' films had a conductivity about 40 times as high as that of the 'no additive' film.

| Level | Surface resistance Ω /sq | Thickness μ m | Electrical conductivity S/cm |
|-------------|------------------------------------|----------------------|---------------------------------|
| No additive | 9391 | 2.7 | 0.41 |
| Additive A | 189 | 3.0 | 17.67 |
| Additive B | 172 | 3.3 | 17.81 |

Table 4: Conductivity of the test films

ESR AND RELIABILITY OF SOLID ELECTROLYTIC TANTALUM CAPACITORS

Table 5 shows the ESR and the reliability of the solid electrolytic tantalum capacitors made of the test conductive polymer solutions.

In the 'no additive' capacitor, the ESR was 39.7 m Ω . The 'additive A' and 'additive B' capacitors had an ESR lower than that of 'no additive' (35.8 m Ω and 38.2 m Ω respectively). In a reliability test on the heat resistance (125 degrees Celsius) and the humidity resistance (65 degrees Celsius, 95% RH) of the test capacitors, the ESR of the 'additive A' and 'additive B' capacitors was always lower than that of the 'no additive' capacitor.

| Level | ESR | High temperature (125°C, 500H) | Humidity test (85°C, 85%R.H.) |
|-------------|----------------|-----------------------------------|----------------------------------|
| No Additive | 39.7m Ω | 81.2m Ω | 35.8m Ω |
| Additive A | 35.8m Ω | 50.1m Ω | 34.8m Ω |
| Additive B | 38.2m Ω | 48.9m Ω | 35.5m Ω |

Table 5: ESR and reliability of the solid electrolytic tantalum capacitors tested

These results indicate that addition of an additive to a conductive polymer can lower the ESR and increase the reliability of the resulting solid electrolytic tantalum capacitor.

XRD OBSERVATION OF THE CRYSTALLIZATION OF TEST FILM SAMPLES

We used XRD to assess the crystallization of the test films. Figure 5 shows the XRD spectra of the test films, as well as the XRD spectra of the 'additive A' and 'additive B' films after subtraction of the 'no additive' spectrum ('additive A - no additive' and 'additive B - no additive'). Two major peaks were observed at $2\theta = 18^\circ$ and 26° in any of the test films. Based on a previous report⁵, the peak at $2\theta = 26^\circ$ derives from the stacking of PEDOT. The peak at $2\theta = 18^\circ$ is attributable to PSS, because it was also prominent in a PSS film (not shown).

The signal intensity was higher in 'additive A' and 'additive B' at almost every angle than in 'no additive' (backgrounds were not included). Thus we examined the spectrum 'additive A - no additive' and the spectrum 'additive B - no additive' to analyze the effect of the additives. The spectra 'additive A - no additive' and 'additive B - no additive' both had the peak at 18° , indicating that additive A and additive B promoted the crystallization of PSS. The peak around 26° was still present in the spectrum 'additive A - no additive', but it was much smaller in 'additive B - no additive'. These results indicated that the different additives differently promoted the crystallization of PEDOT.

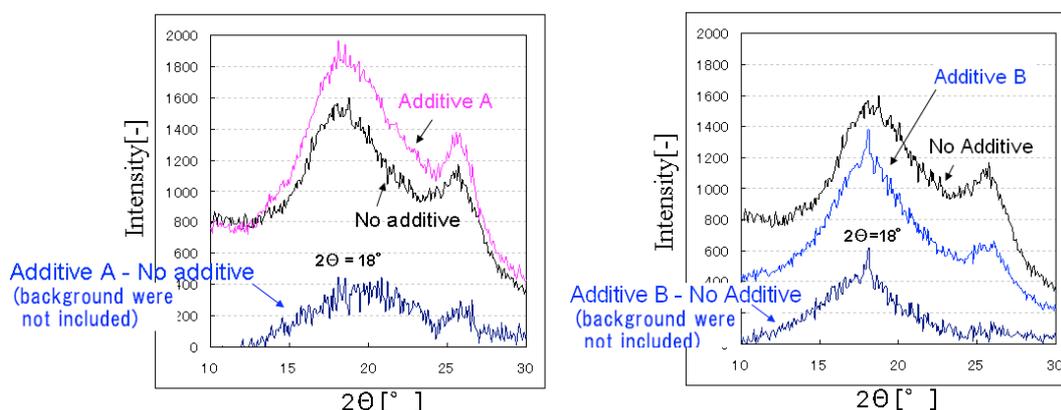


Figure 5: XRD spectra of test samples

XPS MEASUREMENT OF THE PEDOT/PSS RATIO OF TEST FILMS

To examine the distribution of PEDOT and PSS in the test films, their PEDOT/PSS ratios were determined at varying detection depths by XPS. The detection depth was set by appropriately adjusting the photoelectron take-off angle. Figure 6 shows the XPS spectra of the 'no additive' film at different photoelectron take-off angles. Based on a previous report³, the peaks at 168 eV and 164 eV correspond to PSS and PEDOT, respectively. The PEDOT/PSS ratio of each test film was calculated from these two kinds of peak areas. This is a rough calculation because noise level cannot be neglected.

Figure 7 shows the ratio between the PEDOT peak area and the PSS peak area for the 'no additive' film and the 'additive B' film, obtained by XPS. In both films, the ratio increased as the detection depth became deeper (2.4 nm, 3.6 nm, and 4.8 nm). Then, the degree of the ratio is discussed. In the 'no additive' film, however, the PEDOT/PSS ratio at the depth of 2.4 nm was markedly small; i.e. the difference between the PEDOT/PSS ratio at the depth of 2.4 nm and that of 4.8 nm was relatively large. In the 'additive B' film, the difference between the PEDOT/PSS ratio at the depth of 2.4 nm and that of 4.8 nm was smaller compared to 'no additive'. These results indicate that additive B made the PEDOT/PSS ratio more uniform from the depth of 2.4 nm to 4.8 nm of the film.

A previous report⁵ estimated the thickness of the PSS layer to be 37 angstroms by XPS and UPS. In the present study, the PEDOT/PSS ratio at the depth of 2.4 nm to 4.8 nm differed between 'no additive' and 'additive B', suggesting that PSS around the PEDOT:PSS colloid surface had been removed⁴.

The 'additive A' film was not robust enough so that its PEDOT/PSS ratio was not determined. This might be because the 'additive A' solution contained a large amount of additive A, which likely remained on the surface of the dried film.

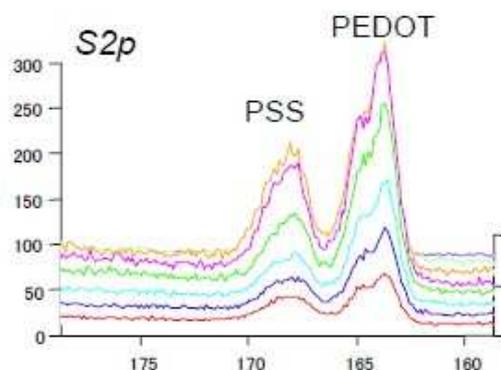


Figure 6: XPS spectra of the 'no additive' film at different take-off angles

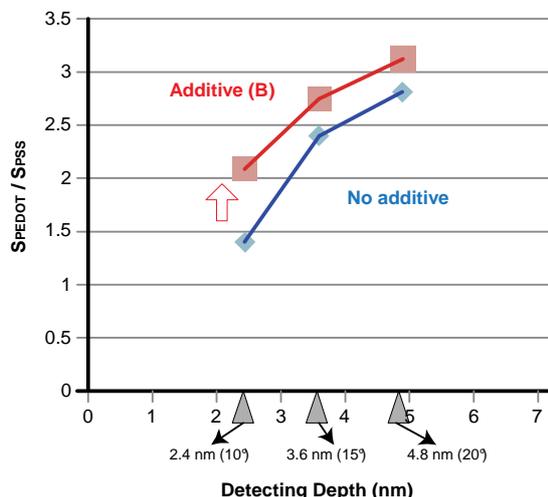


Figure 7: PEDOT/PSS spectrum area ratio at different depths (rough calculation because of noise / coating film thickness: 100 nm)

FT-IR STUDY OF CHEMICAL BOND FORMATION IN THE TEST FILMS

Figure 8 shows the FT-IR results of the test conductive polymer films. In 'additive A' and 'additive B' but not in 'no additive', we observed major peaks near 1700 cm⁻¹ and 1250 cm⁻¹. These peaks correspond to CO double and single bonds respectively, suggesting that ester bonds were formed in the 'additive A' and 'additive B' films.

Among the constituents of the test conductive polymer films, only the additives are capable of ester bond formation. Thus we think that these ester bonds were formed between the additive molecules.

In 'additive A' and 'additive B', the solid electrolytic tantalum capacitors were improved in reliability, i.e. more heat-resistant. This is possibly because the ester bonds formed by the additive molecules in the conductive polymer solution improved the adhesion to the underlayer and the strength of the resulting conductive polymer film.

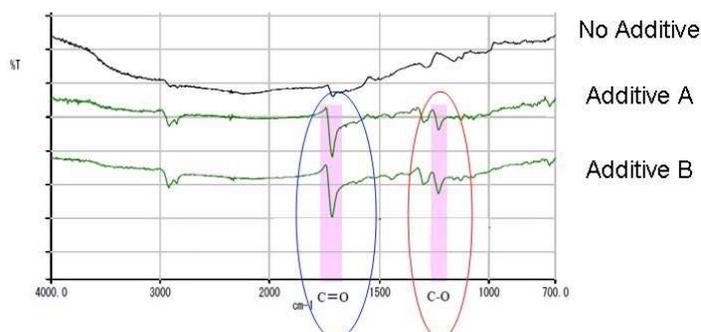


Figure 8: FT-IR spectra of films each made from a conductive polymer solution with or without an additive (additive A or B)

RESULTS SUMMARY

As shown by the conductivity test, additives A and B successfully improved the conductivity of the conductive polymer film to lower the ESR and increase the reliability of the corresponding solid electrolytic tantalum capacitor. The possible underlying mechanisms are discussed below.

As to the improved conductivity, the crystallization was promoted as observed by XRD and the PEDOT/PSS ratio was relatively uniform as observed by XPS in the 'additive A' and 'additive B' films, compared to the 'no additive' film.

The promoted crystallization in the 'additive A' and 'additive B' films likely caused more PEDOT chains to be reoriented so that the electron mobility between the PEDOT chains improved. On the other hand, the relatively uniform PEDOT/PSS ratio in these 'additive' films likely improved the electron mobility between the conductive polymer particles, possibly because insulating PSS molecules on the particle surface were removed.

We propose that the mechanism of the improved conductivity due to additive A or additive B involves the increase in the electron mobility both between the conductive polymer chains and between the conductive polymer particles.

The improved crystallization and the more uniform PEDOT/PSS ratio brought by the additives can be explained as follows. During the drying of the conductive polymer solution, liquefied additive molecules were possibly concentrated in the PEDOT:PSS to weaken the coulomb interaction between the PEDOT and the PSS, thereby causing the reorientation. In the course of the reorientation, the crystallization could be promoted and the PEDOT/PSS ratio could become more uniform.

Newly formed chemical bonds between the additive molecules were observed by FT-IR. It was suggested that the chemical bond formation improved the film properties of the resulting conductive polymer film. The addition of the additives to the conductive polymer solution likely formed films that can strongly adhere to the in situ polymerized conductive polymer layer, thereby reducing the interface resistance.

We suppose that these improved film properties both lowered the ESR and increased the reliability.

CONCLUDING REMARKS

By adding additives to a PEDOT:PSS conductive polymer solution, we have improved the conductivity of the conductive polymer film to successfully produce a solid electrolytic tantalum capacitor with further lowered ESR and increased reliability. Therefore addition of appropriate additives to conductive polymer solutions will make it possible to develop solid electrolytic tantalum capacitors with low ESR and/or high reliability in the future.

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MEMBER COMPANY NEWS

We would like to remind you that articles concerning T.I.C. members or the industry in general are posted regularly on the T.I.C. website in the section entitled '[News](#)'.

CHANGES IN MEMBER CONTACT DETAILS

A&R Merchants

A&R Merchants has changed address. The new address is 1701 NW 93rd Avenue, Doral FL 33172, U.S.A. All other contact details remain the same.

Jiujiang Zhongao Tantalum & Niobium Co. Ltd.

Jiujiang Zhongao Tantalum & Niobium Co. Ltd. has announced a new website address: www.zatanb.com

Mineração Taboca S.A.

Mr Itamar Resende has been nominated CEO of Mineração Taboca S.A. Mr Resende is also a member of the Executive Committee of the T.I.C.

Mitsui Mining & Smelting Co Ltd

Mitsui Mining & Smelting Co Ltd has nominated Mr Jun Sugimura to represent the company within the T.I.C., in the place of Mr Tomotaka Iwai. He can be contacted on j_sugimura@mitsui-kinzoku.co.jp

Thailand Smelting & Refining Co Ltd

Mr Nicholas Thorne, the delegate for Thailand Smelting & Refining Co Ltd, has changed email address. He can now be contacted on nick.thorne@amcgroup.com

EXECUTIVE COMMITTEE

According to the Charter of the T.I.C., the Executive Committee may consist of between two and eleven people, plus the President. The Executive Committee is drawn from the membership, and committee members may be, but need not also be, the delegates of member companies.

The Executive Committee composition was approved by the T.I.C. members at the General Assembly on Monday October 14th 2013, and it now consists of (in alphabetical order):

- John Crawley icrawley@rmmc.com.hk
- Alan Ewart adewart@alance.co.uk
- David Gussack david@exotech.com
- Dale Gwinnutt dalegwinnutt@elitematerial.com
- David Henderson dhenderson@rittenhouseir.com
- Jiang Bin jiangb_nniec@otic.com.cn
- Ian Margerison ian.margerison@metalysis.com
- William Millman bill.millman@avx.com
- Yasukazu Muto yasukazu.muto@hstarck.com
- Daniel Persico (President) danielpersico@rc.jp.nec.com
- Itamar Resende iresende@btinternet.com
- Alexey Tsorayev tsorayeva@ulba.kz

