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Solid-State Anodic Oxidation of Aluminum with Organic-Conductor Counterelectrode

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Solid-state anodic oxidation of aluminum contacted to a pellet of various organic conductors based on 7,7,8,8-tetracyanoquinodimethane was observed. A typical passivation curve was observed in the current-voltage characteristics for the anodic polarization of the metal. Along with impedance measurements on the electrode system, it was proved that the passivation is due partly to a thermal transformation in the organic conductor and partly to a solid-state anodization of aluminum, the latter being conditioned by the former through the formation of an electrolyte layer *in situ*. The current efficiency of anodization was estimated by a linear voltage sweep method to be as high as 2%, depending on the ambient moisture. The high efficiency explains the prominent self-healing action of a new type of solid electrolytic capacitor in which manganese dioxide is replaced by an organic-conductor counterelectrode.

The solid electrolytic capacitor was developed in 1956,[1)] but little experimental information on the anodic oxidation of valve metals with a solid electrolyte has been given since then. Smith[2)] studied the electrical properties of a tantalum electrode pressed on a surface of manganese dioxide, MnO_2, and claimed that the tantalum oxide is anodically formed at the expense of the local oxygen content of MnO_2. There is, however, another theory according to which the counterelectrode functions in the capacitor self healing; a thermally induced transition of the oxide to insulating lower oxides.[3)] Smith did not exclude the thermal reduction of MnO_2 but rather credited it with the appearance of a high electric field appropriate to the ionic conduction.[2)]

Recently a new type of aluminum solid electrolytic capacitor, in which MnO_2 is replaced by organic conductor, OC, was developed.[4)] Highly conductive organic salts based on 7,7,8,8-tetracyanoquinodimethane, TCNQ,[5)] were adopted, because of their prominent effect on the capacitor self healing. The capacitor was featured by stable high frequency characteristics[6)] and a very low leakage current density. In this paper we wish to report on the electrical properties of an Al/OC electrode system, showing that the solid state anodic oxidation proceeds at an efficiency of up to 2%, considerably higher than that with MnO_2. The current-voltage and impedance characteristics of the electrode system, are presented with a discussion on the mechanism of anodic oxidation.

Experimental

Materials. Typical molecular compounds of TCNQ, including non-ionic change transfer complexes and less conductive ion-radical salts with metallic cations were examined. We report herewith on highly conductive salts which might have significance in capacitor application. The effects of resistivity, thermal stability and stoichiometry on the solid state reaction were studied for the compounds, quinolinium-$(TCNQ)_2$, $Q(TCNQ)_2$, *N*-methylquinolinium$(TCNQ)_{2.2}$, $(NMQ)(TCNQ)_{2.2}$, *N*-propylquinolinium$(TCNQ)_2$, $(NPQ)(TCNQ)_2$, *N*-methylacridinium$(TCNQ)_2$, $(NMA)(TCNQ)_2$, and *N*-methylphenazinium(TCNQ), (NMP)(TCNQ). $(NMQ)(TCNQ)_{2.2}$ and (NMP)(TCNQ) were a metastable, highly conductive modification,[7)] the former sample being used to examine the contribution of the thermal transformation of the solid counterelectrode. Results on the salts with metallic cations will be referred to as regards the discussion of the reaction mechanism.

Electrode System. The TCNQ compounds were compressed under a pressure of *ca.* 2000 kg/cm^2 into a pellet of 13 mm in diameter and *ca.* 0.8 mm in thickness. A 99.999% hard aluminum bar, 0.5 mm diam., was used as an electrode metal. This was degreased with 10% NaOH and rinsed with deionized water and acetone. The bar was truncated immediately before measurement and the fresh surface was pressed on the OC pellet. It was extremely difficult to obtain a reproducible contact between Al and OC. The dominant factors for the reproducibility were the nature of the surfaces of both solids, contact pressure and the water content of the pellet. Figure 1 shows a test jig for the Al/OC electrode system, with which a pressure as high as 100 kg/cm^2 could be applied to the contact without any deformation of the bar. Since the glossy surface of the OC pellet did not give a reproducible result, it was rubbed with emery paper and lapped with cotton gauze.

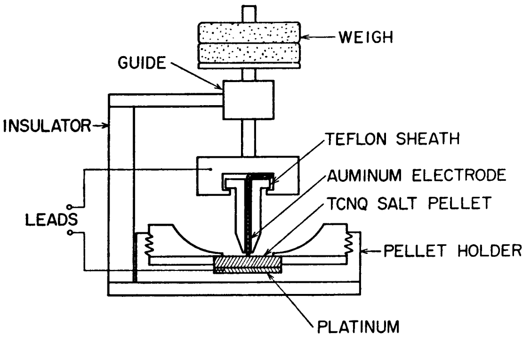

Fig. 1. Sketch of a constant-pressure, point-contact electrode system.

Apparatus. The current-voltage characteristics were measured by the constant-rate-of-voltage-increase (CRVI) method first adopted by Dignam[8)] for the anodic oxidation of Al in a liquid electrolyte. Since a very low rate of voltage increase with a very low noise level is required to meet the supposed low efficiency of the solid state reaction,[2)] we constructed a Miller integrator with operational amplifiers and a 500 μF slug tantalum electrolytic capacitor. Measurements with stepwise application of constant voltage were found to be inappropriate for the OC system, for it was not possible to distinguish between the anodic and the cathodic reactions especially when the thermal transformation of OC took part in the reaction. The impedance of the Al/OC system was measured as a function of the applied voltage with a Yokogawa BV-Z 13A universal bridge at a frequency of 1 kHz. Measurements of the equivalent series capacitance, C_s, and resistance, R_s, were made after the current had reached a steady state for each applied voltage.

Results

Current-Voltage Characteristics. The *I-V* characteristics measured by the CRVI method for three Al/OC systems, shown in Fig. 2, are typical data for a humidity of 50% RH and a voltage rise rate of 1/24 V/s. For the anodic polarization (*e.g.* when Al was anodically polarized), all the electrode systems exhibited a well-known passivation curve with a current peak, V_p^+, between 2.5 and 4.7 V, the current following as low as 10^{-5} A for higher voltages. The curves are very smooth with no discontinuity below *ca.* 15 V, at which the current suddenly diverges resulting in decomposition in OC at the contact point. For the cathodic polarization, there are more than one current peaks, the current making an oscillatory growth. The first peak appears, in all cases, at a lower voltage than the anodic peak. The anodic and cathodic peak voltages and powers ($W_p^{\pm} = V_p^{\pm} I_p^{\pm}$) along with the specific resistivity of compactions[9] for the OC's examined are summarized in Table 1. The superlinear curve in the anodic direction results from a contact resistance at voltages lower than 1 V and the Joule heat above 1 V. In the underlinear and decreasing regions, the change in the electrode resistance is irreversible; the resistance is not restored by the application of cathodic voltage. In the cathodic direction, however, an reversible increase in the electrode resistance takes place from *ca.* 0.1 V, for the resistance is restored by the anodic polarization, provided that the cathodic electrification does not exceed the voltage of the first peak. The difference in the *I-V* characteristics between the anodic and cathodic directions strongly suggests that the passivations are due to electrochemical reactions.

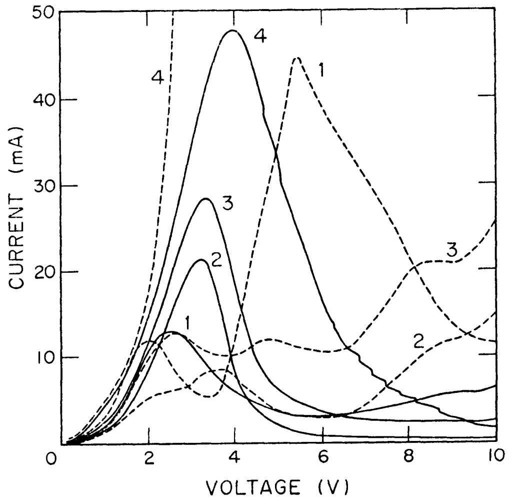

Fig. 2. Current-voltage characteristics at 1/24 V/s and 50% RH of an Al electrode system for anodic (solid lines) and cathodic (dotted lines) polarizations. 1. Q(TCNQ)$_2$, 2. (NPQ)(TCNQ)$_2$, 3. (NMA)(TCNQ)$_2$, 4. MnO$_2$.

TABLE 1. PEAK VOLTAGE $V_p^{\pm}$ AND POWER $W_p^{\pm}$ OF PASSIVATION CURVES

Compound	V_p^+ (V)	W_p^+ (mW)	V_p^- (V)	W_p^- (mW)	ρ (Ω cm)
Q(TCNQ)$_2$	2.5	32.5	2.0	23.6	0.6
(NMQ)(TCNQ)$_{2.2}$	3.3	64.4	2.5	20.0	1.0
(NPQ)(TCNQ)$_2$	3.0—3.2	74.5	2.3	12.7	3.6
(NMA)(TCNQ)$_2$	3.1—3.3	89.1	2.6	33.3	1.3
(NMP)(TCNQ)	4.7	91.2	4.2	52.5	7.8
MnO$_2$	3.8—4.0	568	—	—	5

The results for an Al/MnO$_2$ systems are also shown in Fig. 2. MnO$_2$ was obtained by thermal decomposition of a 50% Mn(NO$_3$)$_2$ solution in the form of a block which was cut and lapped into nearly the same shape as that of the OC pellet. The MnO$_2$ system exhibited essentially the same anodic curves as the OC system, though there were a number of discontinuous falls in current at $V > V_p^+$, indicating thermal transformation in MnO$_2$. The cathodic current, however, increased to infinity (over 200 mA) at *ca.* 2.5 V.

Thermal Transformation in OC. We measured the *I-V* characteristics using Ta and noble metals, Pt and Au. All the electrodes exhibited a large passivation peak similar to those shown in Fig. 2. However, in the case of the noble metal, there was no difference in the *I-V* curves between the anodic and cathodic polarizations. This indicates that, although the anodic passivation in the Al/OC system is peculiar to the valve metal and is of electrochemical nature, it was initiated by some kind of thermal transformation in OC. Figure 3 shows the current and temperature-voltage characteristics of a chromel-almel, Al/OC system, where the current was passed through the thermocouple, 0.5 mm in diameter (Omega Engineering, Inc.), which was pressed on the OC pellet with a Pt bar. The figure illustrates not only the existence of the passivation peak for the non-valve metal system but also the correspondence of the current to the electrode temperature. A current peak appeared at 2.5 and 4.7 V for Q(TCNQ)$_2$

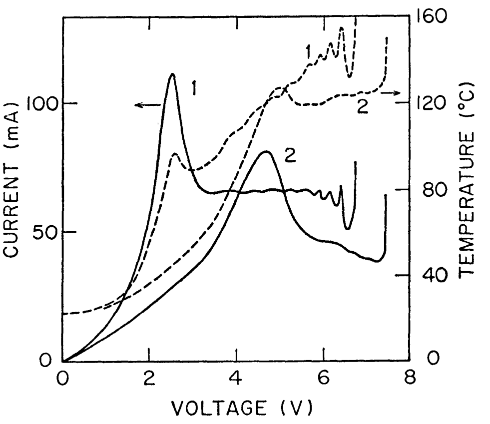

Fig. 3. Current (solid lines)- and temperature (dotted lines)- voltage characteristics at 1/24 V/s and 50% RH of chromel-almel/organic systems.
1. Q(TCNQ)$_2$, 2. (NPQ)(TCNQ)$_2$.

and (NPQ)$(TCNQ)_2$, respectively, and the corresponding temperature peak appeared at 95.7 and 126.4 °C for the former and the latter, respectively. The peak temperatures are considerably lower than the decomposition temperatures of these compounds.[5,10] However, the resistivity of the highly conductive TCNQ salts frequently increases irreversibly at these temperatures.[11] This seems to be due to the dissociation of the neutral TCNQ from the salts.[12] The difference in the position of the current peak or the electric power of the peak (Table 1) between compounds is understandable on the basis of the thermal stability against the dissociation of the compounds.

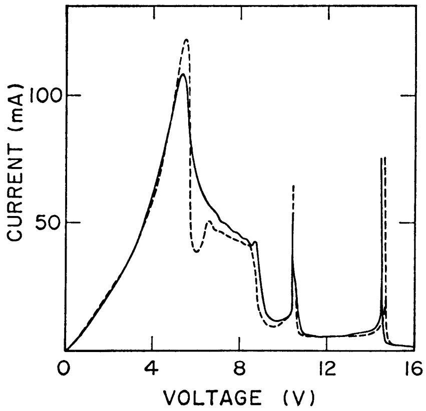

Fig. 4. Current-voltage characteristics at 1/24 V/s of a Pt/(NMQ)$(TCNQ)_{2.2}$ system. —anodic, ···cathodic.

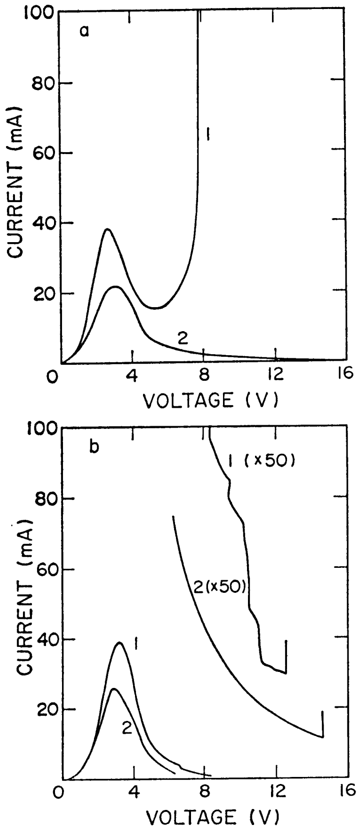

Fig. 5. Effect of humidity on the current-voltage characteristics of Al/Q$(TCNQ)_2$ (a) and Al/(NMA)$(TCNQ)_2$ (b) systems. 1: 20%RH, 2: 98%RH.

Figure 4 shows the *I-V* curves of a Pt/(NMQ)$(TCNQ)_{2.2}$ system forming a single exception in the non-valve metal system. This system displayed drastic decay and spikes in the current starting from *ca.* 8.5 V in addition to the above mentioned passivation at 5.3 V. The metastable modification of (NMQ)$(TCNQ)_{2.2}$ undergoes a monotropic phase transition and the resistivity increases by a factor of 80.[13] The drastic decay (Fig. 4) is undoubtedly due to the phase transition in the bulk of the OC. That the *I-V* curves of Al/(NMQ)$(TCNQ)_{2.2}$ showed no discontinuity implies that the thermal transformation does not dominate at higher voltage ($V \gg V_p^\ddagger$).

Effect of Ambient Moisture. The *I-V* characteristics measured at various relative humidities are shown in Fig. 5. The *I-V* curves in the higher voltage region are severely altered by the ambient moisture. At a relative humidity of 98%RH, the current declines to about an order of magnitude lower than those at 50%RH. In dry air, on the contrary, it increases to infinity with Q$(TCNQ)_2$ or shows lots of jumps with (NMA)$(TCNQ)_2$ at higher anodic voltages. The discontinuous falls for the (NMA)$(TCNQ)_2$ system are strikingly similar to those for the MnO_2 system (Fig. 2), indicating that a thermal transformation proceeds locally in the OC. In the case of Q$(TCNQ)_2$, however,

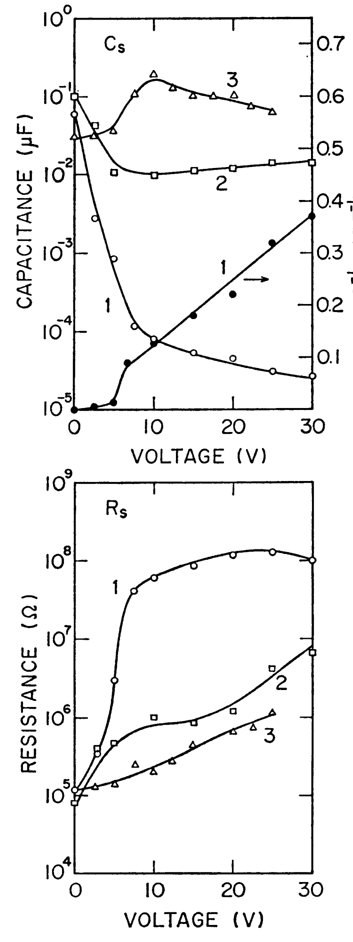

Fig. 6. Equivalent series capacitance and resistance of an Al/Q$(TCNQ)_2$ system. 1: Anodic polarization in the room air (about 70 %RH), 2: anodic polarization in dry oxygen, 3: cathodic polarization in the room air.

the I-V curve and the appearance of the Al contact indicate carbonization in the OC. This seems to be due to the low thermal stability of Q(TCNQ)$_2$. In any case, the results confirm that the anodic passivation should be ascribed to two mechanisms, each being replaced by the other at a voltage of *ca.* $2V_\mathrm{p}^{+}$ in the presence of water. The cathodic I-V curves and the curves obtained using the non-valve metal electrodes are not largely altered by the relative humidity.

Impedance Characteristics. Figure 6 shows C_s and R_s at 1 kHz of the Al/Q(TCNQ)$_2$ system measured under three typical conditions. For the anodic polarization in humid air (about 70%RH), C_s decreases and R_s increases markedly with increasing voltage. The inverse of C_s shows a linear dependence on the voltage at voltages in excess of *ca.* 6 V, the voltage roughly corresponding to that at which the CRVI curve reaches a steady state (Fig. 2). This strongly indicates the formation of the anodic oxide on Al. The very high electrode resistance, R_s, may also be evidence for the anodization, since the thermal transformation alone cannot yield such a high resistance as suggested by curve 2. Curves marked 2 give the result of measurements in dry oxygen. They have almost the same features as those of the non-valve metal systems, so that the measured impedance is thought to be that of the transformed OC alone. It should be noted that the R_s measured at higher RH decreased again at higher voltages; in the case of (NMQ)(TCNQ)$_{2.2}$, for example, R_s decreased to the same value as the initial R_s. The decrease can be explained by the formation of a very high resistance connected in parallel with the anodic capacitor. The cathodic reaction causes an increase in C_s with a slight increase in R_s, indicating that the cathodic passivation is not dominated by the thermal transformation of OC either.

Discussion

Anodic Oxidation. The experimental results on the electrical properties of the Al/OC electrode system as a whole confirm the solid-state anodic oxidation of Al, though no direct evidence for the material transport or the existence of Al$_2$O$_3$ was found. One possible objection may be that there might be an electrochemical reaction of the TCNQ salts followed by a disproportionation reaction with water or *vice versa* at high electric fields. However, if such reaction could take place, the strict relation $C_\mathrm{s}V$=constant (Fig. 6) would be too accidental, since the electrification period was not made constant for each applied voltage. Assuming the electrode area as 2×10^{-3} cm^2, we obtain $C_\mathrm{s}V=0.44$ μF·V/cm^2, which is to be compared with $C\cdot V=6.45$ μF·V/cm^2 for the ideal anodization in a boric acid-borate solution.[14] Coincidence between experiment and theory is considered to be good in view of various factors through which the capacitance is lowered; namely, 1) reduction of the contact area arising from the roughness of the surface, 2) a series capacitance due to the thermally transformed OC, and 3) a low efficiency of the solid-state reaction.

The CRVI method, which was originally introduced for the analysis of the anodic oxidation in the liquid electrolyte,[8] is useful and powerful for the solid state reaction. The anodic and the cathodic reactions are discriminated and different reactions depending upon the voltage are manifested. Let us calculate the current efficiency of the anodic oxidation using the CRVI results.[15] When the ionic current I_i flows through the oxide of thickness x, the equation for an oxide growth rate dx/dt is given by Faraday's law,

$$\mathrm{d}x/\mathrm{d}t = \Omega I_\mathrm{i} \qquad (1)$$

where Ω is 5.55 A s^{-1} mA^{-1} cm^2 for Al$_2$O$_3$. Then the potential across the oxide V_ox increases as follows,

$$\mathrm{d}V_\mathrm{ox}/\mathrm{d}t = E_v\mathrm{d}x/\mathrm{d}t \qquad (2)$$

where E_v is the Maxwell field strength which depends on the rate of voltage increase v. If we assume

$$\mathrm{d}V_\mathrm{ox}/\mathrm{d}t = \mathrm{d}V_\mathrm{a}/\mathrm{d}t = v \qquad (3)$$

where V_a is the applied voltage and define the ionic current efficiency η with respect to the total current I through the electrode system as

$$I_\mathrm{i} = \eta I, \qquad (4)$$

then we obtain from Eqs. 1 through 4,

$$\eta = v/\Omega E_v I. \qquad (5)$$

Since Eq. 3 holds for $V_\mathrm{a}\gg V_\mathrm{p}^{+}$ or for I_i=constant, η can be calculated using the experimental data on I in Fig. 2. The results for a relative humidity of 50%RH are shown in Table 2, where E_v was obtained by Dunn[15] as $E_v=8\times10^6$ V/cm for $v=1/24$ V/s. The efficiency was found to be 0.05 to 1.7%, considerably higher than the published data on the Ta/MnO$_2$ system (0.01 to 0.001%).[2] At higher relative humidities, the efficiency was higher; 2.1% for Q(TCNQ)$_2$ and 1.5% for (NMA)(TCNQ)$_2$ at 98%RH. The efficiency for the MnO$_2$ system cannot be obtained, since the discontinuous falls in the I-V curves do not allow us to assume Eq. 3. An apparent efficiency was calculated to be 0.93% at 14 V, which is thought to be an overestimate by about two orders of magnitude over a true value if we take the amount of the discrete jumps in current into account.

TABLE 2. CURRENT EFFICIENCY OF ANODIC OXIDATION, η (%), AT 50% RH

Compound	η (Voltage, V)
Q(TCNQ)$_2$	0.053 (6)
(NMQ)(TCNQ)$_{2.2}$	1.68 (13)
(NPQ)(TCNQ)$_2$	0.62 (13)
(NMA)(TCNQ)$_2$	0.10 (13)
(NMP)(TCNQ)	0.21 (16)

Reaction Mechanism. The anodic oxidation necessitates both an ionically conducting layer which prevents the short circuiting of the electrode system and ionogens which may serve as an oxygen source of Al$_2$O$_3$. The TCNQ salts are known as an electronic conductor. The idea of Gutmann *et al.*[16] that Mg(TCNQ)$_2$ behaves as a solid electrolyte has been vitiated by Friedel[17] and Weidenthaler and Pelinka.[18] We postulate that the initial passivation at relatively low voltages (V_p^{+}) produces an ionically conducting layer between Al and OC. Since the transformed layer has a higher resistivity, the applied voltage may be absorbed by this thin layer, resulting in a high electric field effective to the ionic conduction. The TCNQ salts we examined meet the requirement for the anodizing electrolyte postulated by Smith.[2] The transformed OC was dissolved in acetonitrile and the composition was determined spectroscopically.[7] It was shown that the layer contains an excess of neutral TCNQ molecules over a stoichiometric composition; *e.g.*, TCNQ/cation=2.11 for the transformed NPQ salt. The resulting nonstoichiometric compound is very advantageous for anodic oxidation. First, the disordered structure may give a good chance for the ionic conduction as in the case of inorganic materials.[19,20] Second, the OC layer with excess TCNQ molecules may behave as a p-type conductor,[21] to facilitate rectification of a junction $Al/Al_2O_3/OC$.[22]

It was assumed in the above discussion that the existence of neutral TCNQ is essential for anodization. For the sake of comparison simple salts with metallic cations, such as Li, Na, K, Mg, Ca, Ba, Mn(II), Fe(II), Ni(II), and Cu(I) were examined. However, they were not anodizing electrolytes for the valve metals. The only metallic salt which exhibits both a passivation curve in the CRVI experiment and a remarkable decrease in C_s in the impedance measurement is $Cu(TCNQ)_2$. An X-ray photoemission study[23] and IR study have shown that $Cu(TCNQ)_2$ is not a simple salt but is composed of Cu(I)(TCNQ) and $TCNQ^0$ as a formulation of $Cu^+(TCNQ^-)(TCNQ^0)$ or $(Cu^+)_2(TCNQ^-)_2(TCNQ^0)_2$,[5] providing another support for our model. The anodizing ability of the simple salt (NMP)(TCNQ) is not counterevidence either. A recent examination has revealed a partial charge transfer between NMP and TCNQ,[24] suggesting the existence of $TCNQ^0$. This may explain the striking difference in the anodizing ability between (NMP)(TCNQ) and alkali-TCNQ's, the charge transfer being complete in the latter.[24] The results and those with $(NMQ)(TCNQ)_{2.2}$ suggest that nonstoichiometric salts having higher contents of TCNQ[25] may be a more efficient anodizing electrolyte.

Since the TCNQ salts we examined have no oxygen in their composition, water should be the oxygen source. It is not unreasonable because water is, with a few exceptions,[26] the oxygen source in most of the anodic oxidation in liquid electrolyte. The findings of Weidenthaler and Pelinka[18] that the presence of water is essential for the electromotive force to be observed in a cell, metal/TCNQ-salt solution/Pt, should also be considered. Smith's claim that water is a catalyst in the anodic oxidation of the Ta/MnO_2 system cannot be accepted. The major electrochemical reactions are the dissociation of water and/or the oxidation of Al, and the efficiency may vary with the catalytic activity of $TCNQ^0$ in the electron transfer processes. In fact, the formation of an ion pair Al···TCNQ with the aid of water has been known[27] and a slowly decreasing electromotive force was generated in a cell Al/OC/Pt with Al negative.

Conclusion

The experimental results as a whole support the anodic oxidation of Al with the OC functioning as a solid electrolyte *in situ*. The material criteria for the anodizing electrolyte are that the existence of neutral TCNQ molecules in the salt is essential and the disordered structure is favored. The high efficiency of anodization explains the prominent self-healing action of a new type of solid electrolytic capacitor in which MnO_2 is replaced by an OC counterelectrode.[4]

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