The use of PAS capacitors / lithium capacitors for adapting to diversification of energy supply

Introduction of energy devices for adapting to diversification of energy supply

Electrochemical capacitors (hereinafter, 'capacitors') have previously been used as an alternative to batteries for their strong performance in low temperatures. Recently, they have come to be used in new ways, making use of their other characteristics, such as reduced environmental load substances, longevity of the charge-discharge cycle and durability in rapid charge-discharge.

Taiyo Yuden offers various capacitors from 30 mF to 200 F (as seen in Figure 1) that accommodate all types of energy requirements. Examples include lower capacity products suitable for backing up IC in real time clock and higher capacity products suitable as an alternative for secondary batteries connecting to photovoltaic cells.

In this article, we will describe the features of our polyacene capacitors (PAC) and lithium-ion capacitors (LIC).

Diversifying Requests for Energy Devices

Requests for energy devices in handsets are becoming more diversified recently. More handheld terminals that previously used coin type lithium non-rechargeable or rechargeable batteries for backing up the RTC or memory are beginning to employ capacitors for reasons of environmental awareness or the need for reflow soldering during assembly.

Higher energy density rechargeable batteries, such as lithium-ion secondary batteries, are widely used as power sources in cellular phones, laptops and other mobile devices. In fact, we could even say that development of those batteries was what enabled such devices to become so common. In some cases, however, these batteries do not have a fast response speed during charge and discharge because their energy density is large enough but the power density is not.

Capacitors are used in applications where such power density is crucial, such as LED flash or for temporary large currents exceeding the supply power in USB equipment by charging electricity when the load is low and discharging when needed.

Used with photovoltaic cells, capacitors are able to store small amounts of electricity generated from photovoltaic cells even when it is cloudy or rains.

PAS Capacitors

Square Type/Coin Type PAS Capacitors

Square type and coin type PAS capacitors are mainly used for backing up the RTC in handsets (such as cellular phones).

These are used in RTC backup as they are thin and small and can withstand reflow soldering.

Taiyo Yuden offers various thin, small square type and coin type PAS capacitors that can be reflow soldered thanks to their excellent heat resistance of PAS-electrodes and higher energy density.

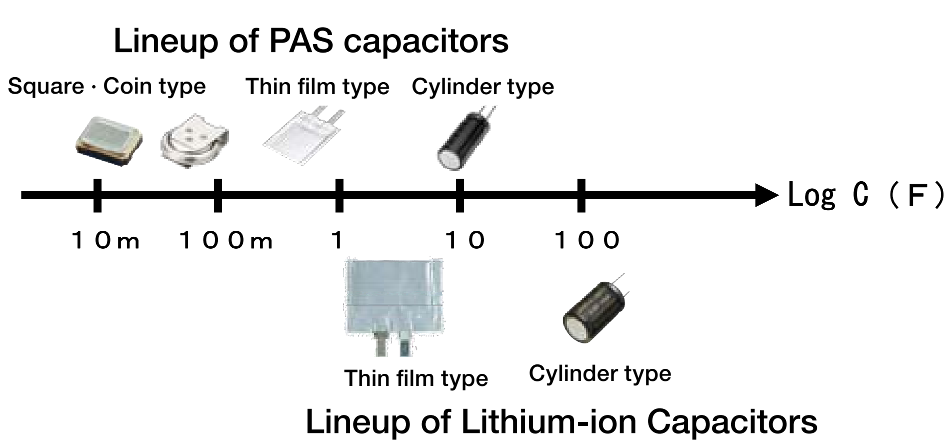


Figure1　Product line of Taiyo Yuden's PAS/LIC Capacitors

Features of PAS capacitors

Main features of PAS capacitors are listed below.

①High Value

Higher energy density is achieved compared to conventional electric double-layer capacitors as the capacitors use polyacene (PAS) obtained from heat-condensing phenol resin as the positive/negative terminals and charge or discharge with ions in the electrolytic solution doping or undoping to the PAS.

Capacitors differ from secondary batteries in that they do not have a charging voltage threshold at the redox potential and can be charged or discharged at any voltage under the maximum (ranging from 2.5 V to 3.5 V in the products). (Figure 2)

②Longevity in Charge/Discharge Cycle

The cycle life is long because the structural alteration of the electrode material is very small compared to that of secondary batteries. (Figure 3)

③Heat-Resistance in Reflow

By using thermally-stable polyacene as electrodes, the heat-resistance in the inorganic-material separators and the package are enhanced. (Square types use ceramic material and coin types use gaskets which have high heat-resistance.)

In addition, reflow soldering with a Pb-free solder paste that is eco friendly is made possible with our encapsulating technology.

Taiyo Yuden's latest specifications of square/coin type PAS capacitors are shown in Table 1.

Low and high voltage type capacitors are offered in different sizes as square-shaped low voltage types and coin-shaped Pb-free reflowable types. (SR, HR)

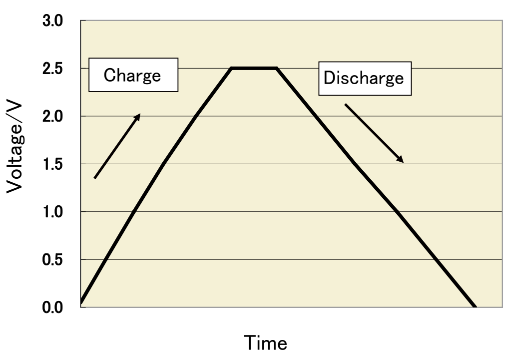


Figure2 Charge/Discharge Curve of a PAS Capacitor

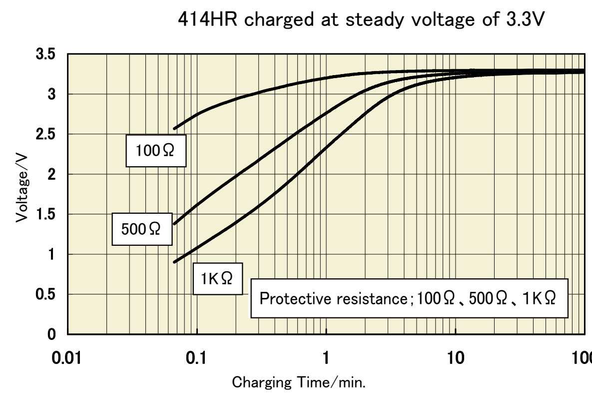


Figure4 Charge Characteristics of PAS414HR

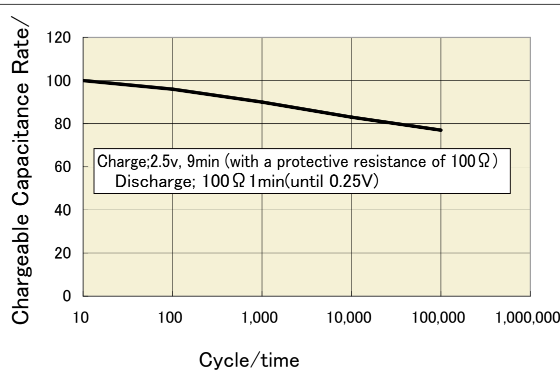


Figure3 Change of Chargeable Capacitance Rate in Cycle

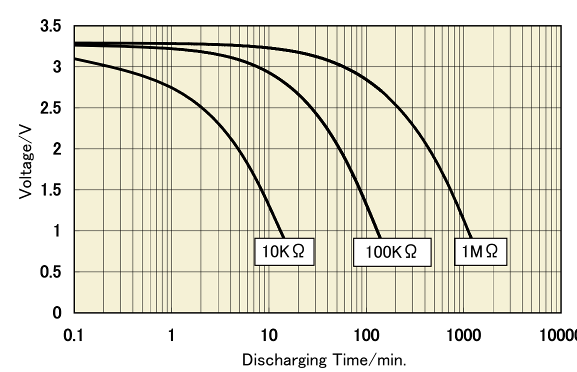


Figure5 Discharge Characteristics of PAS414HR

Part Number	Height(H) mm	Outside(φ) diameter Width(W) mm	Thickness(T) Height (H) mm	Rated Voltage (V)	Capacitance (F)	Energy Capacity mAh	Internal Resistance (typ) Ω	High Temperature Loaded Characteristics Guarantee Time h	Change rate of Capacitance %	Internal Resistance %	Operating Temperature Range ℃
Coin type Capacitor											
PAS311SR		3.8 φ	1.1	2.6	0.03	0.010	50	500	>70	<400	-25～70
PAS311HR		3.8 φ	1.1	3.3	0.03	0.010	120	500	>70	<400	-20～60
PAS409SR		4.8 φ	0.9	2.5	0.04	0.010	50	500	>70	<400	-25～70
PAS409HR		4.8 φ	0.9	3.3	0.03	0.012	100	500	>70	<400	-20～60
PAS414TR		4.8 φ	1.4	2.0	0.08	0.022	80	500	>70	<400	-25～70
PAS414SR		4.8 φ	1.4	2.5	0.07	0.018	50	500	>70	<400	-25～70
PAS414HR		4.8 φ	1.4	3.3	0.06	0.020	80	500	>70	<400	-20～60
PAS614L		6.8 φ	1.4	3.3	0.25	0.090	160	500	>70	<400	-20～60
Square type Capacitor											
PAS3225P 2R6143	3.2	2.5	0.9	2.6	0.014	0.0045	80	500	>70	<400	-30～70

Table1 Product line and Specs of Square/Coin type PAS Capacitors

In addition, we also offer a Lithium-dope type (L) that can be soldered manually and features high-voltage and high-capacitance and a square type capacitor, which has less mounting space and is reflowable with PB-free solder paste.

The charge and discharge properties of PAS414HR, a typical product of PAS, are shown in Figures 4 and 5.

Cylinder/Thin-film Type PAS Capacitors

Like coin type capacitors, by using polyacene (PAS) obtained from heat-condensing phenol resin as filmy positive/negative terminals, these products are able to feature high capacitance with low ESR as the electrolytic ions are easily doped and undoped to the polyacene.

Some of Taiyo Yuden's cylinder/thin film type PAS capacitors are shown in Figure 6.

Products and rated voltages of the cylinder type low ESR PAS (LR), high capacitance PAS (LA) and thin-film type PAS (FR) are shown in Table 2.

As seen in this Table, LR types achieve low ESR characteristics even with low value capacitance.

Figure6 Cylinder/Thin film type PAS Capacitors

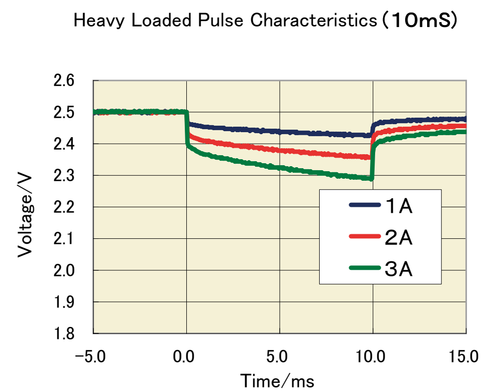


Figure7 Heavy Loaded Pulse Characteristics of a Low ESR-PAS Capacitor(ϕ8×15:1F)

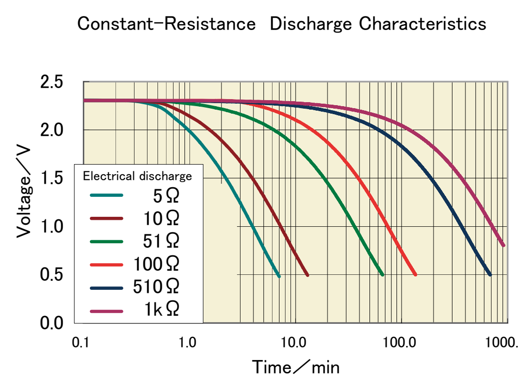


Figure8 Discharge Characteristics of High value Capacitors(ϕ18×40:50F)

The discharge curve of the LR series for discharge of a large current pulse is shown in Figure 7.

As seen in Figure 7, similar to the LR series, some newly developed smaller sized of capacitors have less of a voltage-drop when a large current pulse is discharged even with low capacitance. This enables their use in various situations such as handling load changes during discharge or backing up data during emergencies.

LA series high capacitance PAS capacitors can also achieve high capaci-

Part Number	Height(H) mm	Outside(ϕ) diameter Width(W) mm	Thickness(T) Height (H) mm	Rated voltage (V)	Capacitance (F)	Energy Capacity mAh	Internal Resistance (typ) Ω	High Temperature Loaded Characteristics: Guarantee Time h	Change rate of Capacitance %	Internal Resistance %	Operating Temperature Range ℃
Cylinder type PAS Capacitor LR series(Low-ESR)											
PAS0815LR2R3105		8 φ	15	2.3	1	0.64	0.07	1000	>70	<400	-25〜60
PAS1016LR2R3205		10 φ	16	2.3	2	1.28	0.05	1000	>70	<400	-25〜60
Cylinder type PAS Capacitor LA series(Large current)											
PAS1020LA2R3475		10 φ	20	2.3	4.7	3.0	0.3	1000	>70	<400	-25〜60
PAS1220LA2R3106		12.5 φ	20	2.3	10	6.4	0.2	1000	>70	<400	-25〜60
PAS1235LA2R3226		12.5 φ	35	2.3	22	14.1	0.1	1000	>70	<400	-25〜60
PAS1840LA2R3566		18 φ	40	2.3	56	35.8	0.07	1000	>70	<400	-25〜60
PAS1020LA3R0405		10 φ	20	3.0	4	3.3	0.3	1000	>70	<400	-25〜60
PAS1220LA3R0905		12.5 φ	20	3.0	9	7.5	0.2	1000	>70	<400	-25〜60
PAS1235LA3R0206		12.5 φ	35	3.0	20	16.7	0.1	1000	>70	<400	-25〜60
PAS1840LA3R0506		18 φ	40	3.0	50	41.7	0.07	1000	>70	<400	-25〜60
Thin Film type Capacitors											
PAS2126FR2R5504	21	26	0.9	2.5	0.5	0.35	0.08	500	>70	<150	-25〜60

Table2 Product line and Specs of Cylinder/Thin Film type PAS Capacitors

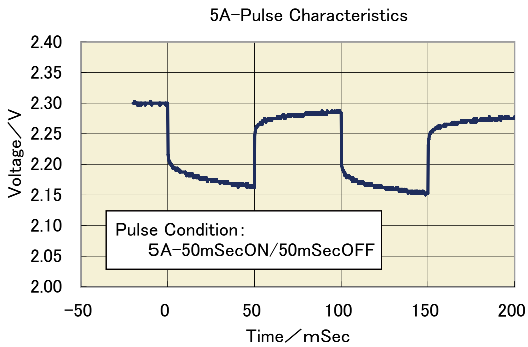


Figure9 Heavy Loaded Pulse Characteristics of a High Value Capacitor(ϕ18×40:50F)

tance with low ESR. As seen by the discharge characteristics and heavy load pulse characteristics in Figures 8 and 9, we offer various types of capacitors for applications that require high capacitance or high power density (for example in handling fluctuations in discharge loads or in charge loads during energy regeneration).

Moreover, the LA series includes a 3V type with improved rated voltage thanks to use of specially-treated PAS electrodes combined with an electrolytic solution composition.

In addition, thin-film PAS capacitors are also offered for assistance to secondary batteries in handsets or backing up the power supply of Solid State Drives (SSDs).

Application of PAS Capacitors

The above features of PAS capacitors will likely be applied to expand their use from simple substitutes for small batteries to use in handsets where they can obtain energy rapidly.

Specifically, the below applications are considered, some of which are already in practical use.

① Use as an alternate power source for backing up RTCs

② Use in large currents such as LED-flash

③ Use for peak-assistance in USB devices

④ Use as a power source in SSD and other system backups

Lithium-ion Capacitors

Lithium-ion Capacitors (LIC) are hybrid capacitors with features of both EDLC and lithium-ion secondary batteries (LIB). They are being developed in more and more companies for their benefits of high energy density, reliability, longevity and safety.

In this article, we describe the features and characteristics of LICs in comparison with the symmetric type EDLC.

Principles and Features of LICs

LICs are hybrid capacitors which use a carbon-based material as the negative electrode that can be doped with lithium. For the positive electrode, it can use either activated carbon that is used in conventional EDLCs or polyacene-organic semiconductors. The basic concept of the principles of LIC are depicted in Figure 10. Metallic lithium, electrically connected to the negative electrode, forms a local battery at the same time as immersion of the electrolytic solution. Then, doping of lithium ions begins on the carbon-based material at the negative electrode. Once doping is complete, the initial voltage of the LIC drops to 3V or less as the electric potential of the negative electrode almost matches that of lithium.

Therefore, as seen in Figure 11, compared to the charging/discharging potential of conventional EDLCs, a higher voltage can be obtained by using LICs without a high potential at the positive electrode, which results in improved reliability in LICs.

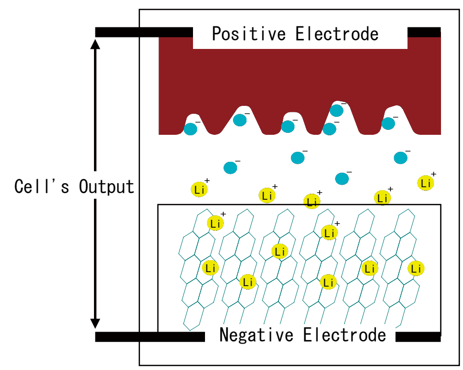


Figure10 Principle of LIC

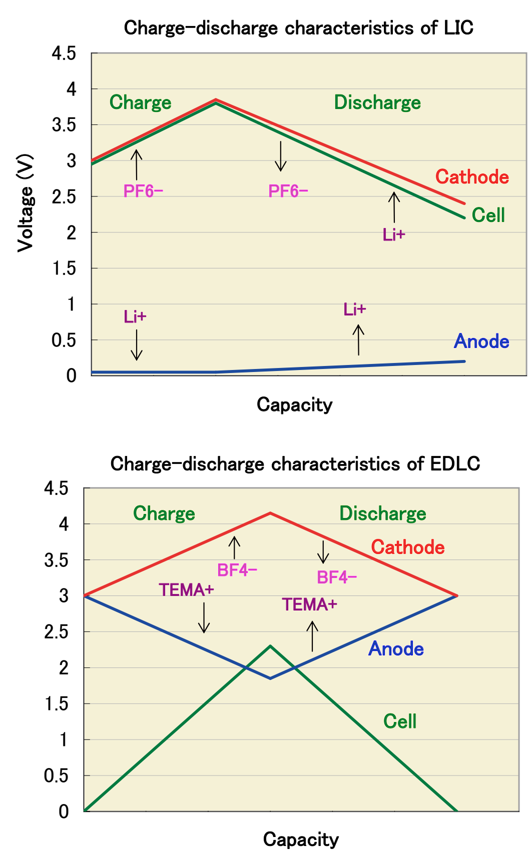


Figure11 Charge/Discharge Voltage Characteristics of LIC and Symmetrical EDLC

Cylinder/Thin-film Type PAS Capacitors

Taiyo Yuden's lineup of LICs is shown in Table 3.

As seen in this Table, the maximum voltage of LICs, 3.8 V, is higher than that of a symmetric type EDLC, and the capacitance is twice that of the EDLC. Therefore, the energy density of LIC is quadruple that of the EDLC, based on the formula of "Q=1/CV2".

①Characteristics of Discharge Rate

Figure 12 shows the discharge characteristics of a cylinder type LIC with 200F in a wide range of discharge current. As the capacitance of this LIC is about 100 mAh at the range of 3.8 V to 2.2 V, the LIC has a strong characteristics in discharge at the rate of 1C to 100C.

As it can obtain about 60% of the discharged capacity at a discharge rate of 100C, the LIC can be said to be a capacitor with excellent discharge characteristics in high output.

Figure 13 shows a Ragone plot comparison of a cylinder type LIC with 200F and a conventional symmetric EDLC whose size is similar to the LIC. The energy density of the LIC is 9.8WH/kg, far larger, about 6.5 times larger, than the 1.5Wh/kg. of the conventional EDLC.

②Temperature Characteristics

Figure 14 shows the temperature characteristics of the cylinder type LIC with 100F at the discharge of 100 mA (2C rate). A stable discharge curve is obtained even at high temperatures and a volume-maintenance rate of over 60% is achieved even at a low temperature of -20ºC. In addition, a strong volume-maintenance rate of about 50% is achieved at extremely low temperatures, even when affected by the voltage drop caused by lesser mobility of ions in the electrolytic solution. With that, we would say that the LIC has good temperature characteristics.

③ Self-discharge Characteristics

One major feature of the LIC is its excellent 'self-discharge property,' which is enabled by pre-doping of lithium to the negative electrode to stabilize the potential of the negative electrode.

Figure 15 shows the self-discharge property of the cylinder type LIC with 40F charged for 24 hours in 3.8 V at a temperature of 25ºC and those of a symmetrical type EDLC whose capacitance is similar to the LIC.

As seen here, the symmetrical type EDLC has a large self-discharge. After a month under 25ºC, its voltage lowered to 80% of the initial voltage. In contrast, the LIC shows far better self-discharge. It can maintain a voltage of over 3.7 V even 100 days later under a temperature of 25ºC.

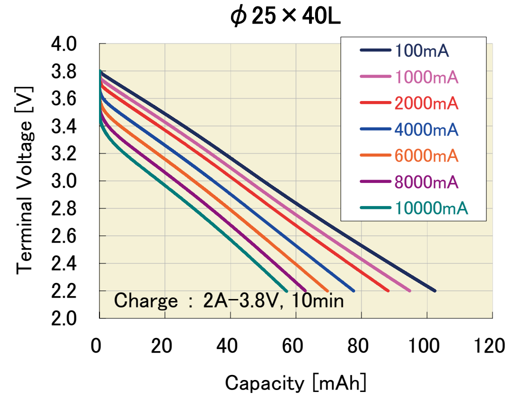


Figure12 Discharge Rate Characteristics of Cylinder type LIC(ϕ25×40:200F)(25℃)

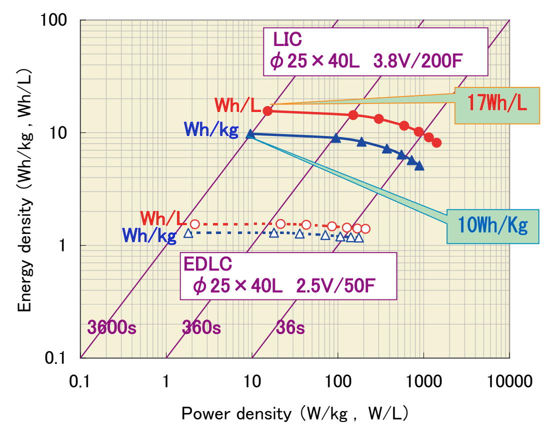


Figure13 Ragone plot of LIC(25℃)

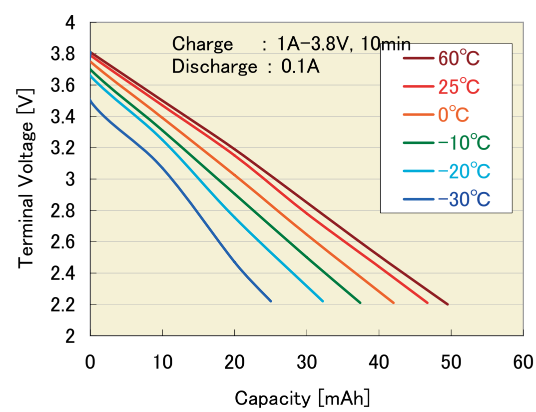


Figure14 Temperature Characteristic of LIC

Part Number	Height(H) mm	Outside(ϕ) diameter Width(W) mm	Thickness(T) Height (H) mm	Rated voltage (V)	Min.Voltage (V)	Capacitance (F)	Energy Capacity mAh	Internal Resistance (typ) Ω	High Temperature Loaded Characteristics: Guarantee Time h	Change rate of Capacitance %	Internal Resistance %	Operating Temperature Range ℃
Cylindrical Lithium Ion Capacitor												
LIC1235R 3R8406		12.5 φ	35	3.8	2.2	40	18	0.15	1000	>70	<400	-25～60
LIC1840R 3R8107		18 φ	40	3.8	2.2	100	44	0.10	1000	>70	<400	-25～60
LIC2540R 3R8207		25 φ	40	3.8	2.2	200	89	0.05	1000	>70	<400	-25～60
Thin Lithium Ion Capacitor												
LIC3527F 3R8135	35	27	0.45	3.8	2.2	1.3	0.58	1	- - -	>70	<200	- - -
LIC3527F 3R8605	35	27	1	3.8	2.2	6.0	2.67	1	- - -	>70	<200	- - -

Table3 Product line and Specs of LIC

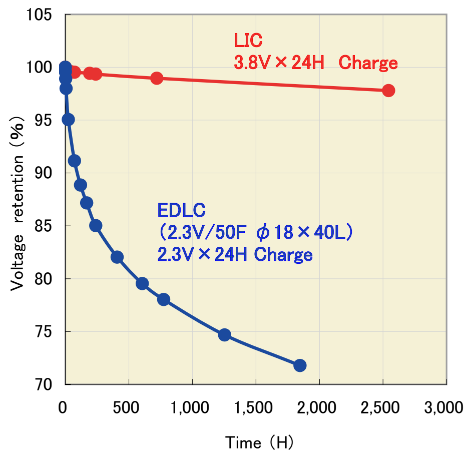


Figure15 Comparison of Self Discharge characteristics Between LIC and Symmetrical EDLC(25℃)

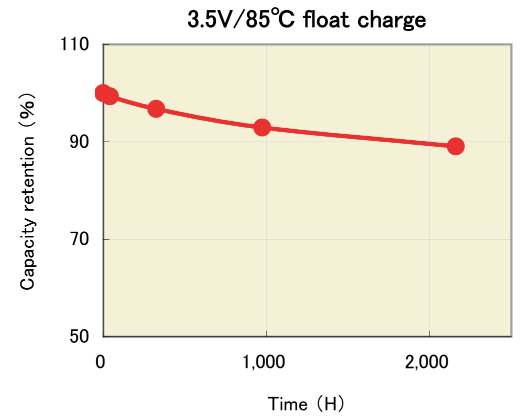


Figure17 High Temperature Loaded Characteristics of LIC(Change rate in capacitance at 85℃-3.5 V consecutive charging)

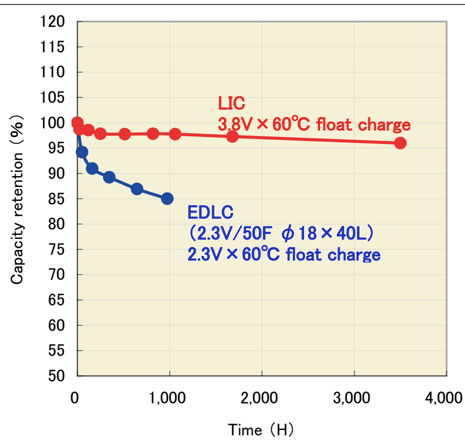


Figure16 High Temperature Loaded Characteristics of LIC and Symmetrical EDLC(Change rate in capacitance at 60℃ celsius consecutively charging rated voltage)

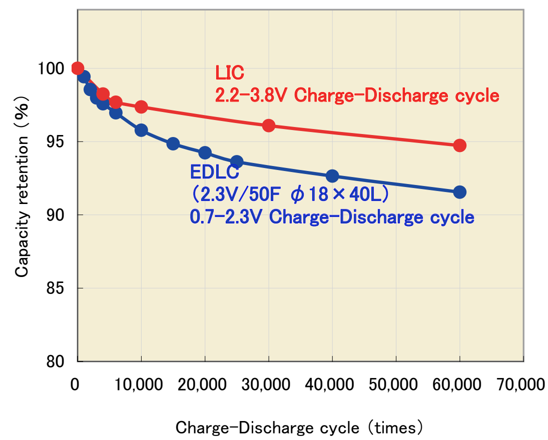


Figure18 Charge-Discharge Cycle characteristics of LIC and symmetrical EDLC

④Float Charge Characteristics

Figure 16 shows the float charge characteristics (consecutive-charge) of a cylinder type LIC and symmetrical EDLC whose capacitance is almost similar to the LIC under a temperature of 60ºC.

As mentioned in "Principles and Features of LICs", one of the features of lithium-ion capacitors is that even with a high voltage charge of 3.8 V, the capacitors can lower their potential at the positive electrode to less than that of conventional symmetrical EDLC, which prevents their float charge from deteriorating and makes them highly reliable.

Moreover, as seen in Figure 17, charged at 3.5 V, the float charge characteristics (consecutive-charge) of a cylinder type LIC under a high temperature of 85ºC shows good results with about 90% of the initial voltage maintained even 2000 hours later.

⑤Charge/Discharge Cycle Characteristics

Unlike lithium-ion secondary batteries, LICs are chemically-stabilized products that employ the adsorption-desorption reaction of ions so that they do not cause a crystalline change at the positive electrode during the charge-discharge cycle.

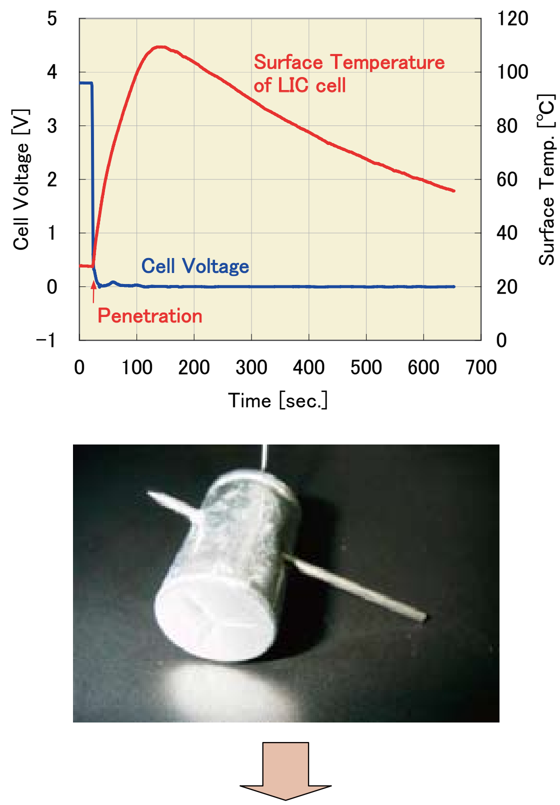
In addition, lithium is doped to a carbon-based material of the negative electrode in advance and the LIC can be designed to lower the lithium ions availability in the negative electrode. This gives the LIC to excellent charge/discharge cycle characteristics of over 100 thousand times, equivalent to that of conventional symmetrical type EDLCs.

Some of these applications are already in practical use.

Safety of LIC

Using a carbon-based material doped by lithium ions at the negative electrode may give you concern about the safety, similar to LIBs (Lithium Ion battery). However, the materials of their positive electrodes are utterly different: LIB uses metal oxide and LIC uses carbon-based materials such as activated carbon, which does not contain oxygen. This differentiates their reactions when an internal short-circuit occurs.

In LIBs, when an internal short-circuit occurs, the temperature of the internal cell rises by the short-circuit current. A following reaction between the negative electrode and the electrolytic solution causes an increase in the pressure of the internal cell, followed by a collapse of the crystal at the positive electrode and a release of oxygen in oxidation products of the positive electrode. This causes another thermal runaway, and, in some cases, an ignition or



No Open and Swollenness in the Safety Valve

Figure19 Safety Test Result of LIC

an explosion might occur due to a further rise in pressure of the internal cell and vaporization of the electrolytic solution.

In contrast, the internal pressure of the cell also rises in LICs, but after that, thanks to the difference of the materials in the positive electrodes (LICs do not contain oxygen), the thermal runaway phenomenon will not occur and the reaction quietly finishes with the opening of safety valves.

Thus, LICs will not cause any serious accidents such as fires or explosions by the thermal runaway even of an internal short-circuit or other accident occurs, thanks to the difference of the material of its positive electrode compared to LIBs. LIC can be said to be as logically safe an energy device as conventional non-aqueous solvent based EDLCs.

Figure 19 shows the results of a nail penetration test to a cylinder type LIC with 200F, assuming an actual internal short-circuit.

These results show that the LIC is a safe device. Even if the temperature of an external wall of the cell increases to 100ºC after short-circuiting, the temperature gradually decreases and the cell does not cause serious problem such as major deformations or explosions.

With these results, LIC is a good device equivalent to the symmetrical type EDLC in safety, has a number of features such as that it does not cause the thermal runaway even with rising internal cell temperatures, unlike LIBs, it does not contain any metal oxides as a material of the positive electrode. In addition, if an internal short-circuit should occur, internal short-circuits from an elution in base materials of the negative electrode are unlikely as the potential of the negative electrode does not exceed the elution potential of Cu.

LIC Applications

Small to mid sized LICs, with their features, are likely to be used as devices that can contribute to reducing the environmental load and by their eco-friendly materials and longevity as electric components, combined with renewable energies such as solar power generation.

Thin-film type LICs could likely be used with a rapid/concise charge system like an non-contact power transmission and in handsets or communication devices by charging renewable energies.

LIC application fields include:

①Power sources for small appliances, applying the quick rechargeable, lightweight, and low self-discharge features.

Testing Methods	Testing Conditions	Criteria	Test Results
Stabbing a Nail	Charged at 3.8V and penetrated with a nail of Φ2.5mm at the center of the cell vertically then left more than 6 hours	No Explosion or Fire	No Open and Swollenness in the Safety Valve
Forced Charging (Reverse Charging)	Charged until the voltage of 250% of rated voltage with a current density of 50 C	No Explosion or Fire	No Open and Swollenness in the Safety Valve
Over Charging	Charged until the voltage of 250% of rated voltage with a current density of 50 C	No Explosion or Fire	No Open and Swollenness in the Safety Valve

The criterion conforms to the lithium rechargeable battery safety criterion guideline (industry association of the battery).

Table4 Summary of Safety Evaluation on LIC(200F)

②Communication systems in meters & reading-meters

③Energy devices combined with photovoltaic cells or wind power generators (such as raised markers, light-emitting load signs, street lights, small LED illuminations)

④Auxiliary power devices for energy saving devices (such as rapid drum heating in copiers and on star-up for projectors)

⑤Computerized devices for automobiles (such as idling-stop devices, drive recorders and brakes by wire)

Some of these applications are already in practical use.

Differences in Use of PAS Capacitors and LICs

PAS capacitors and LICs have separate distinctive features.

Features of these capacitors are shown in Figure 20, and applications suited for the characteristics of each capacitor are shown in Figure 21.

Square/coin type PAS capacitors, which are structurally reflowable with PB-free solder paste, are suited for uses with low energy consumption with moderate output characteristics, such as power sources for backing up RTCs.

Although cylinder/thin-film type PAS capacitors are lower in capacitance than LIC, they can meet requirements for steep output characteristics.

Specifically, they are suited for use in circuits with relatively short intervals between the charge and discharge that need large and steep current such as LED flash, as an assistance of power feeding from the main power supply.

On the other hand, with the LIC's features of low self-discharge and high capacitance with low ESR, cylinder/thin-film type LICs are suited to use as an alternative of batteries, whose charge and discharge are very severe.

Specifically, they are suited for use in circuits with relatively long intervals between the charge and discharge that need high capacitance, such as appliances with solar batteries, regeneration devices or alternatives for conventional standby functions in appliances.

Taiyo Yuden will meet various requirements in power feeding with our extensive product line.

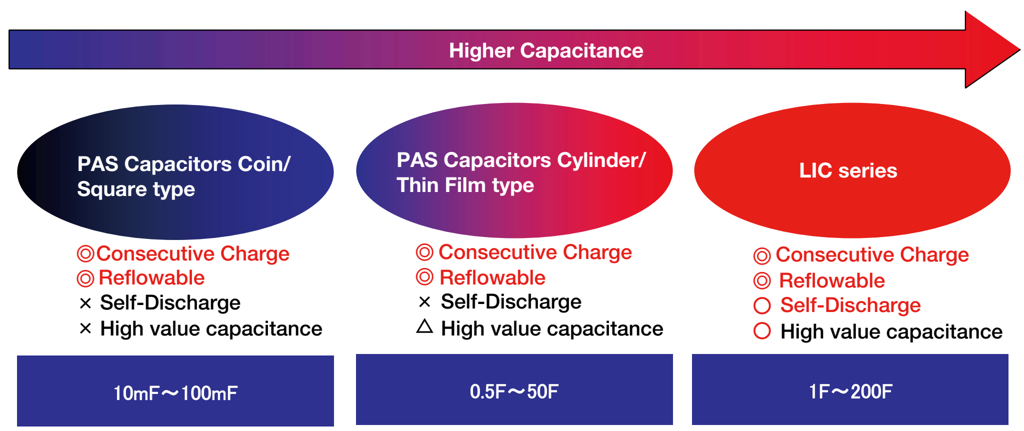


Figure20 Differences in Usage of PAS Capacitors and LICs

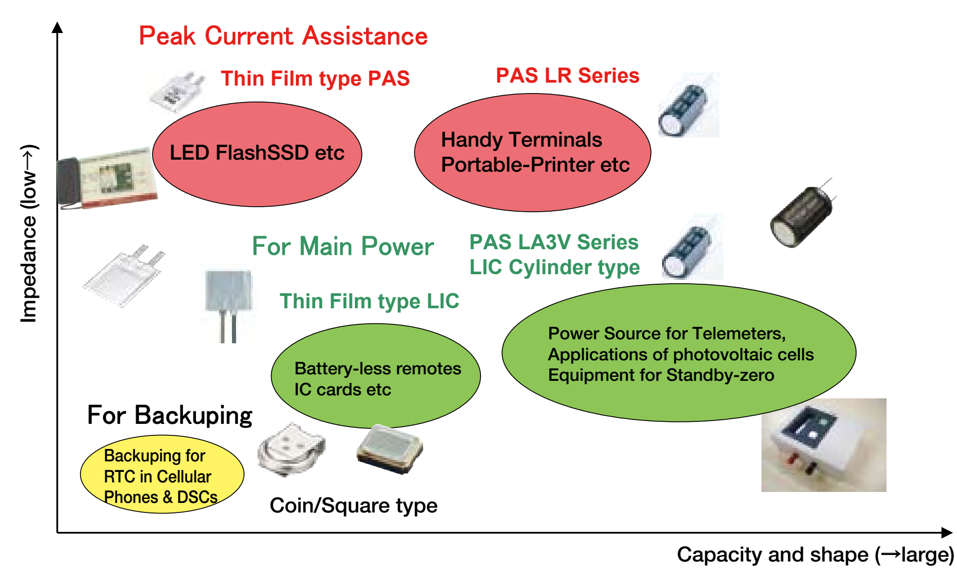


Figure21 Application of PAS capacitor and LIC