



Analysis of electrodes matching for asymmetric electrochemical capacitor

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ABSTRACT

Asymmetric electrochemical capacitor was categorized into two types: a battery-type electrode|capacitor-type electrode capacitor and a capacitor-type electrode|capacitor-type electrode capacitor. When designing asymmetric electrochemical capacitor, the influences of both current density and the electrode's potential window were taken into account. This article analyzed how the mass ratio between two electrodes influenced the electrochemical performances of asymmetric electrochemical capacitor. The formulas describing capacitor performance parameters (work voltage, specific capacitance, energy density and power density) were derived and applied to two types of asymmetric electrochemical capacitors. Therefore, the concrete relationships between mass ratio of electrodes and capacitor parameters were obtained. The influence of current density on mass ratio was investigated with organic $\text{LiMn}_2\text{O}_4/\text{AC}$ system and others.

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1. Introduction

Asymmetric electrochemical capacitor, also called asymmetric hybrid energy storage cell [1–3], consists of different electrochemical active materials to construct its positive electrode and negative electrode. According to the principle of electrochemical active materials, asymmetric electrochemical capacitor can be assigned into two types: battery-type|capacitor-type capacitor and capacitor-type|capacitor-type capacitor. The former type is composed of a battery-type electrode and a capacitor-type electrode. The battery-type electrode is made of materials such as lithium intercalation component, $\text{Ni}(\text{OH})_2$, graphite, etc. The latter is composed of different capacitor materials with different electrochemical windows (ESW) to construct its electrodes. The capacitor-type electrode is made of materials such as activated carbon, multiwalled carbon nanotubes, conducting polymer, etc.

Owing to the asymmetric potential changes of electrodes, an asymmetric electrochemical capacitor possesses a much higher work voltage, larger specific capacitance and energy density. Therefore, great attention has been given to it in recent years. At present, electrodes, used in the asymmetric electrochemical capacitor, involve a large scope of electrochemical materials with diverse work mechanisms and performance disparities, such as aqueous $\text{MnO}_2/\text{Fe}_3\text{O}_4$ system operating at a work voltage of 1.8 V with its energy density of 7 Wh kg^{-1} [4], aqueous $\text{MnO}_2/\text{activated carbon (AC)}$ system at a voltage of 2.2 V with its energy density of 21.0 Wh kg^{-1} [5], aqueous LiMn_2O_4 (LMO)/AC system, 1.8 V,

35 Wh kg^{-1} [6]; non-aqueous manganese oxide-MWNTs composite/MWNTs hybrid capacitor, 2.7 V, 32.91 Wh kg^{-1} [7].

As the result of adopting various types of electrode materials with different influence on the overall performance of an electrochemical capacitor, the matching effect between positive and negative electrode appears. If electrodes are matched well, the overall performance of an electrochemical capacitor will be improved. Otherwise, its performance may drop or the capacitor may be damaged.

For the matching problem of asymmetric electrodes, investigations have been made in recent years. An asymmetric electrochemical capacitor with poly(methyl) thiophene as positive electrode and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as negative electrode was introduced by Pasquier et al. [8]. In their research, the influences of matching mass ratio on Ragone plot and the self-discharge behavior were investigated. The limitations of energy density of battery/double-layer capacitor asymmetric cells were demonstrated by Zheng [9], which illustrated that the swing voltage, specific capacitance and energy density are functions of electrodes' mass ratio, volume ratio and ion concentration of electrolyte.

In this paper, the matching problem of asymmetric electrodes was discussed in detail. Firstly, the influences of current density and electrode's potential windows were analyzed, which may be called current matching and potential matching; secondly, some formulas were developed during mathematical analysis about asymmetric capacitor, and the relationship between mass ratio and capacitor parameters of two categories of asymmetric capacitors was ascertained, such as work voltage, specific capacitance, energy density and power density. At the same time, the concrete influences of current density on capacitor parameters were discussed through examples of organic LMO/AC system and others.

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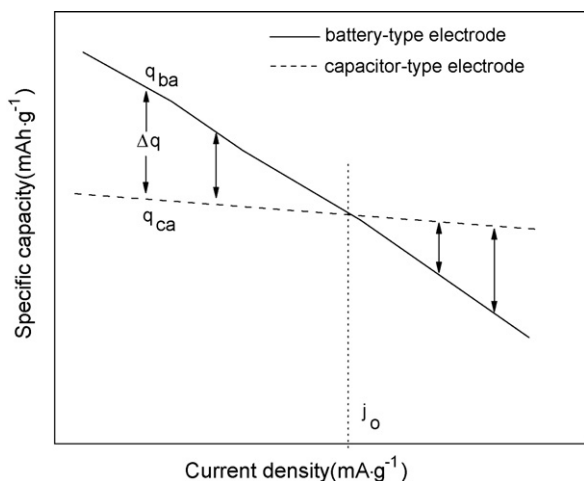


Fig. 1. The schematic curves of specific capacity vs. current density.

2. Analysis of electrode matching

The fundamental of electrode matching which was achieved by adjusting electrodes' mass ratio on the basis of electrodes' specific capacity ratio, is Coulomb-equation between electrodes during charge and discharge processes.

Battery-type electrode and capacitor-type electrode are termed as *ba* and *ca*, respectively; Q (mAh) and J (mA) are the capacity and current of a capacitor, respectively; q_{ba} and q_{ca} (mAh g^{-1}) are the specific capacities of battery-type and capacitor-type electrodes, respectively; j_{ba} and j_{ca} (mA g^{-1}) are current densities of battery-type and capacitor-type electrodes, respectively.

x is the mass ratio of two electrodes and the capacity Q of a capacitor can be expressed as:

$$Q = m_{ba}q_{ba} = m_{ca}q_{ca}, J = m_{ba}j_{ba} = m_{ca}j_{ca} \Rightarrow x = \frac{m_{ba}}{m_{ca}} = \frac{q_{ca}}{q_{ba}} = \frac{j_{ca}}{j_{ba}} \quad (1)$$

$q_{ba, re}$ and $q_{ca, re}$ are rated specific capacities of each electrode material and the capacity matching ratio x_{re} is expressed as:

$$x_{re} = \frac{q_{ca, re}}{q_{ba, re}} \quad (2)$$

2.1. Influence of current density on electrode matching (current matching)

It should be noted that the current density (or current rate) at which specific capacities of electrodes are the basis of electrode matching is always neglected. However, it is of significant importance. The extent of capacity change of each electrode differs along with charge/discharge current, so capacity matching ratio x_{re} is not constant at various charge/discharge currents. In view of the influence of current density on each electrode capacity change, the capacity matching may be termed current matching. Fig. 1 schematically shows specific capacity change status of each electrode with charge/discharge current density. Specific capacity q_{ca} (mAh g^{-1}) of capacitor-type electrode is generally less than q_{ce} (mAh g^{-1}) of battery-type electrode at small current density j (mA g^{-1}). However, the decrease of each electrode's capacity differs when the current density gradually rises. So here is a crossing between two curves in Fig. 1 at a certain current density marked j_o .

The charge/discharge rate limit of a battery-type electrode is actually lower than that of a capacitor-type electrode and the capacity of a battery-type electrode decreases rapidly at a large charge/discharge rate (e.g. LMO), which decays capacitor perfor-

mance and shortens cyclic life. So the content of a battery-type electrode should be excessive on the basis of calculation value of capacity matching ratio.

In view of capacity matching, the mass ratio is in inverse proportion to rated specific capacity ratio of each electrode. It can be known from Fig. 1 that:

- (1) When $j < j_o$, $q_{ba} - q_{ca} > 0$, and $q_{ba} - q_{ca} > \Delta q$. The actual specific capacity approaches to the rated specific capacity of each electrode material when the current density is lower and lower.

$$x = \frac{m_{ba}}{m_{ca}} = \frac{q_{ca}}{q_{ba}} = \frac{1}{1 + \Delta q/q_{ca}} < 1$$

where, x is the mass ratio of electrodes and the capacity matching is calculated at the same current density to each electrode. However, it is actually the same for each electrode except for $j = j_o$. When $j < j_o$, $m_{ba}/m_{ca} < 1$. Current density of a battery-type electrode is bigger than that of a capacitor-type electrode. The actual specific capacity of a battery-type electrode is thereby smaller than matching value calculated above. So the content of a battery-type electrode should be increased.

- (2) When $j = j_o$, the specific capacity of each electrode is the same. Therefore, the mass ratio of electrodes is: $x = m_{ba}/m_{ca} = q_{ca}/q_{ba} = 1$;
- (3) When $j > j_o$, $q_{ba} - q_{ca} < 0$, then $x = m_{ba}/m_{ca} = q_{ca}/q_{ba} = 1 + \Delta q/q_{ba} > 1$. In fact, the current density of a battery-type electrode is smaller than that of a capacitor-type electrode. Thus, actual capacity of a battery-type electrode is bigger than the capacity matching value calculated above.

2.2. Influence of potential change range on electrode matching (potential matching)

Current matching is taken into account in view of the influence of current density on each electrode capacity. It is much more direct to understand the capacity matching problem of asymmetric electrochemical capacitor from the point of view of relationship between capacitor voltage and each electrode's potential, which could be called potential matching. In this paper, double-layer capacitor materials and Faraday pseudocapacitive materials are classified to capacitor-type electrode materials. If the capacitor employs the same capacitor-type electrode material as its two electrodes, it belongs to a symmetric capacitor.

Battery-type electrode's potential keeps platform during charge/discharge process, while capacitor-type electrode's potential changes linearly with charge/discharge time. The latter is considered as a nearly ideal polarization electrode, e.g. activated carbon. A battery-type|capacitor-type capacitor makes use of a battery-type electrode to increase its voltage, energy density and improve its self-discharge behavior; meanwhile it utilizes a capacitor-type electrode to keep a high power density and a long cyclic life, which can be considered as the compromise of electrochemical capacitor and battery [10]. Once electrode materials are appointed, capacitor voltage range is fixed mainly. Then, matching mass ratio should be adjusted to accomplish optimal performance.

Capacitor voltage can be adjusted accurately by regulating matching mass ratio. In terms of capacity matching, each electrode's potential will accord with its ESW. As a result, capacitor voltage will reach a peak value.

When the mass content of a battery-type electrode exceeds, that is to say, if a capacitor-type electrode is fully charged while the battery-type electrode has not yet fully charged, as shown in Fig. 2(a), the change range of a capacitor-type electrode potential accords with its ESW and the potential of a battery-type electrode

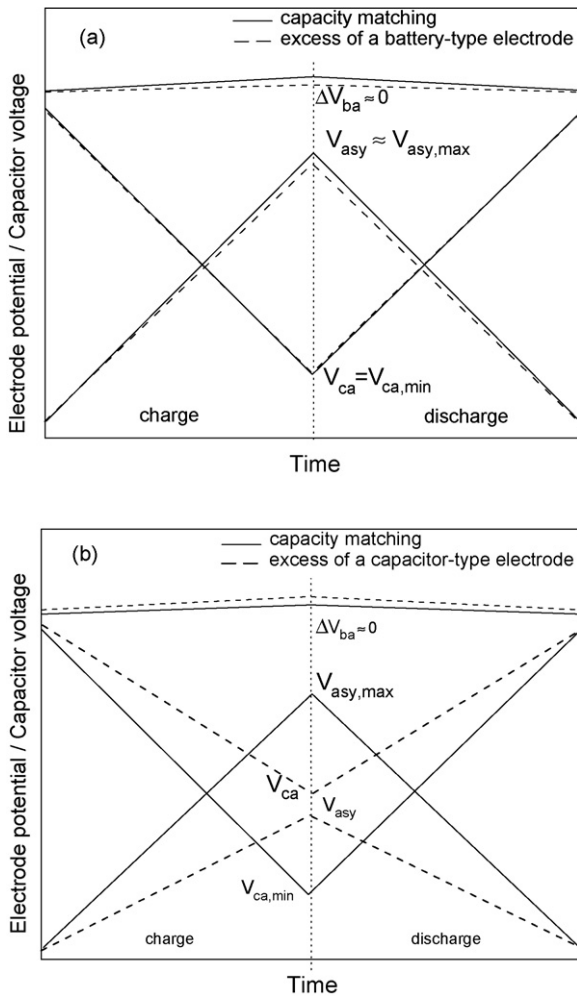


Fig. 2. The scheme of Galvanostatic charge/discharge curves (a) excess of a battery-type electrode, (b) excess of a capacitor-type electrode.

changes little. Under this condition, capacitor voltage equals a peak value approximately.

When content of a capacitor-type electrode exceeds, its potential change range becomes narrow in the same Coulomb charge because of its electric double-layer property. The battery-type electrode can be fully charged and the capacitor-type electrode can not be fully charged, then the charge cutoff potential rise up from $V_{ca,min}$ to V_{ca} as shown in Fig. 2(b). However, the potential change range of a battery-type electrode changes little. Consequently, the capacitor voltage is lower than maximum value $V_{asy,max}$.

When the capacitor is at work, both electrode potentials should be controlled in each ESW and starting potential and ending potential of both electrodes should be dominated for avoiding some invalid charge/discharge processes. Otherwise, the capacitor may be damaged. During charge/discharge processes, the battery-type electrode's potential should be held at a platform value so as not to over-charge or over-discharge and the capacitor-type electrode's potential should not be too high or too low, or else some side reactions such as electrolyte oxidations, lithium plating, etc. Take the organic LMO/AC system for example.

Fig. 3 shows Galvanostatic charge/discharge curves of organic LMO/AC system. The LMO electrode's potential nearly keeps 4 V (vs. Li^+/Li) platform. AC electrode's potential is controlled between 4 V and 1 V (vs. Li^+/Li) in Fig. 3(a), which is in AC's ESW. The specific capacitance is 140.5 F g^{-1} , the energy density is 49.4 Wh kg^{-1} and the Coulomb efficiency was 95.9%. In Fig. 3(b), the potential

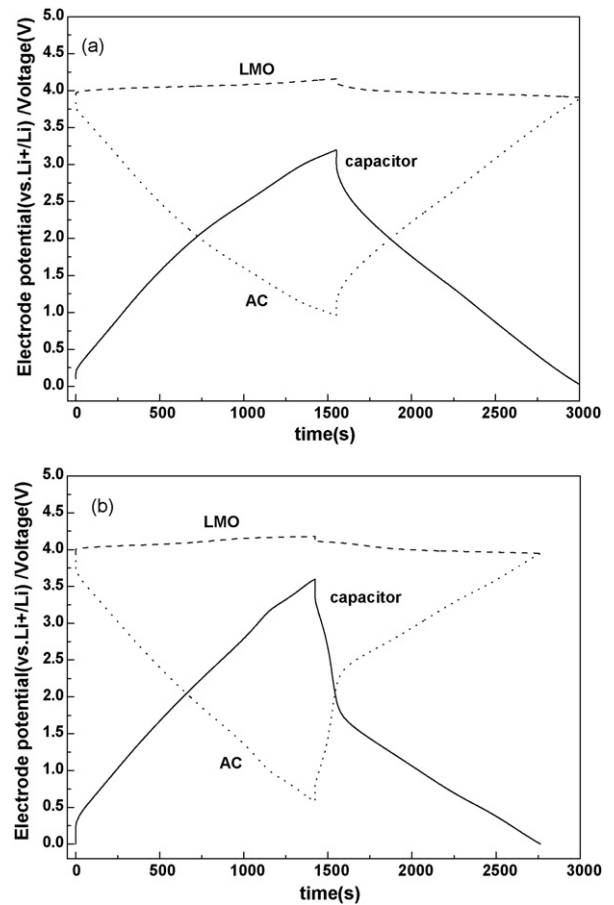


Fig. 3. Galvanostatic charge/discharge curves of the organic LMO/AC system (a) AC potential $\geq 1.0 \text{ V}$ (vs. Li^+/Li), (b) AC potential $\geq 0.6 \text{ V}$ (vs. Li^+/Li).

of AC electrode varies between 4 V and 0.6 V, which is out of its ESW. The specific capacitance is 104.4 F g^{-1} , the energy density is 45.2 Wh kg^{-1} , and the Coulomb efficiency is 77.3%.

3. Calculation on the performance of an asymmetric electrochemical capacitor

Formulas describing the capacitor parameters such as cell voltage, specific capacitor, energy density and power density were derived. Fig. 4 shows schematic potential and capacitor voltage

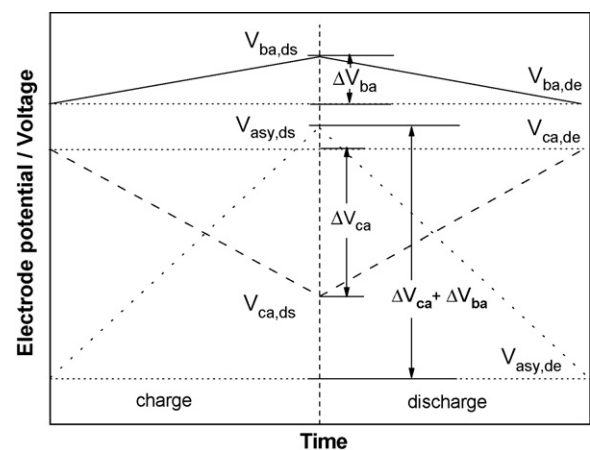


Fig. 4. The scheme of Galvanostatic charge/discharge curves of an asymmetric electrochemical capacitor.

changes during charge/discharge process. To simplify calculation, some assumptions are made as follows:

- (1) the resistance of a capacitor-type electrode is small to neglect, so $IR=0$; the extent of polarization of battery-type electrode is so mild that it could be considered that the charge platform is the same as the discharge platform;
- (2) the Coulombic efficiency is close to 100%;
- (3) a capacitor-type electrode potential change is linear and the slope of the charge/discharge plot is constant; a battery-type electrode's potential change little and the slope of the charge/discharge plot is approximately zero;
- (4) only the influence of electrode potential change and matching mass ratio on performance of a capacitor are taken into account. In other words, capacity of a battery-type electrode and capacitance of a capacitor-type electrode vary little with current density. The influence of current density will be discussed later.

Symbols in Fig. 4:

$V_{ba,ds}$ ($V_{ba,de}$) and $V_{ca,ds}$ ($V_{ca,de}$) represent discharge starting (ending) potentials of a battery-type electrode (*ba* hereafter) and a capacitor-type electrode (*ca* hereafter), respectively; $V_{asy,ds}$ and $V_{asy,de}$ represent the voltage range of a capacitor, namely, the differences of discharge starting and ending potentials of two electrodes.

3.1. Capacitor voltage

$$V_{asy,ds} = (\Delta V_{ca} + \Delta V_{ba}) + V_{asy,de} \quad (3)$$

$$V_{asy,de} = |V_{ba,de} - V_{ca,de}| \quad (4)$$

When electrode materials are confirmed, $V_{asy,de}$ is a fixed value. For a battery-type|capacitor-type capacitor, when the mass content of battery-type electrode is excessive, $x > x_{re}$,

$$V_{asy,ds} = \Delta V_{ca,max} + \Delta V_{ba} + V_{asy,de} \quad (5)$$

When the mass content of capacitor-type electrode is excessive, $x > x_{re}$,

$$V_{asy,ds} = \frac{3.6q_{ba}}{C_{ca}}x + \Delta V_{ba} + V_{asy,de} \quad (6)$$

For a capacitor-type|capacitor-type capacitor,

$$\text{when } x > x_{re}, \quad V_{asy,ds} = \Delta V_{ca,max} \left(\frac{k^2}{x} + 1 \right) + V_{asy,de} \quad (7)$$

$$\text{when } x < x_{re}, \quad V_{asy,ds} = \Delta V_{ba,max} \left(\frac{x}{k^2} + 1 \right) + V_{asy,de} \quad (8)$$

Here, for the consistency of context, “*ba* (*ca*)” is also termed as a capacitor-type electrode with the comparatively bigger (smaller)

capacitance in a capacitor-type|capacitor-type capacitor ($C_{ca} < C_{ba}$). When *ca* and *ba* electrode materials are determined, *k* is constant, $C_{ca}/C_{ba} = k^2$, and $0 < k < 1$.

3.2. Specific capacitance of asymmetric capacitor

$C_{asy,av}$ (Fg^{-1}) is the specific capacitance of an asymmetric capacitor and it is represented as

$$C_{asy,av} = \frac{C_{asy} (F)}{m_{ba} + m_{ca}} = \frac{1}{1 + (\Delta V_{ba}/\Delta V_{ca})} \cdot \frac{1}{1 + (m_{ba}/m_{ca})} C_{ca} \quad (9)$$

For a battery-type|capacitor-type capacitor, $\Delta V_{ba}/\Delta V_{ca} = 0$, when $x > x_{re}$, the content of *ba* electrode is excessive, $C_{asy,av} < \frac{1}{1+x_{re}} C_{ca}$;
when $x > x_{re}$, the content of *ca* electrode is excessive, $\frac{1}{1+x_{re}} C_{ca} < C_{asy,av} < C_{ca}$.

From the above formula, it can be seen:

- (1) for a battery-type|capacitor-type capacitor, its specific capacitance is smaller than that of its capacitor-type electrode;
- (2) the more the mass content of the battery-type electrode exceeds, the smaller the specific capacitance of this type of cell is;
- (3) the specific capacitance of this type of capacitor when the mass content of its capacitor-type electrode exceeds is bigger than that of this capacitor when its battery-type electrode exceeds; the more its capacitor-type electrode exceeds, the bigger the specific capacitance of this type of asymmetric capacitor is.

For a capacitor-type|capacitor-type capacitor, $C_{asy,av}$ can be obtained by taking Eq. (8) into Eq. (9):

$$C_{asy,av} = \frac{1}{1 + (k^2/x)} \frac{1}{1 + x} C_{ca} = \frac{1}{1 + k^2 + (x + (k^2/x))} C_{ca} \quad (10)$$

$$\begin{aligned} \therefore x + \frac{k^2}{x} &\geq 2\sqrt{x(k^2/x)} = 2k \quad (\text{when } x = k^2/x, \\ &\text{viz. } x = k, \text{ it gets minimum}) \\ \therefore \text{when } x = k, \quad (C_{asy,av})_{\max} &= \frac{1}{(1+k)^2} C_{ca} \quad (11) \\ &= \frac{1}{\left(1/\sqrt{C_{ca}} + 1/\sqrt{C_{ba}}\right)^2} \end{aligned}$$

$(C_{asy,av})_{\max}$ is the maximum specific capacitance value of a capacitor-type|capacitor-type capacitor which can be achieved at $x = k$, $(m_{ba}/m_{ca} = \sqrt{C_{ca}/C_{ba}})$.

When electrode materials are confirmed, *k* is constant and matching mass ratio *x* is fixed, $\Delta V_{ba}/\Delta V_{ca} = k^2/x$ is known. In other

Table 1
Values used in calculations, which were either measured independently or taken from literatures.

	Electrolyte	Electrode material	Potential range (V)	Specific capacity (mAh g ⁻¹)	Specific capacitance (F g ⁻¹)	x_{re}
Battery-type (+)/capacitor-type (-)	Organic	LMO	3.7–4.3	120	135	0.75
		AC	3.4–1.0	90		
	Organic	LMO	3.7–4.3	120	120	0.442
		AC	3.4–1.8	53		
Capacitor-type (+)/battery-type (-)	Aqueous [6]	LMO	1.0–1.2	80	180	0.5
		AC	0.2 to -0.6	40		
	Organic	AC	3.2–4.4	40	120	0.108
		Graphite	0.3–0.05	370		
Capacitor-type (+)/capacitor-type (-)	Organic [11]	PFPT	3.5–4.5	40	140	0.312
		LTO	1.6–1.5	125		
	Aqueous [5]	MnO ₂	0.47–1.19	32	160	0.474
		AC	0.47 to -0.88	67.5		
Organic [4]	MnO ₂	0.5–1.0	20.8	150	1.303	
	Fe ₃ O ₄	0.5 to -0.8	27.1			

word, when x is fixed, capacitor voltage with maximum specific capacitance can be known. If electrode materials are the same, it is a symmetric capacitor, that is, $C_{ca} = C_{ba}$, $x = 1$ and $k = 1$. Therefore, the specific capacitance of a capacitor is 1/4 of that of one electrode's specific capacitance.

3.3. Energy density of asymmetric capacitor

$$E_{asy,av(max)} (\text{Wh kg}^{-1}) = \frac{1}{7.2} C_{asy,av} (\text{F g}^{-1}) V_{asy,ds}^2 (V^2) \quad (12)$$

$$E_{asy,av(real)} (\text{Wh kg}^{-1}) = \frac{1}{7.2} C_{asy,av} (\text{F g}^{-1}) (V_{asy,ds}^2 - V_{asy,de}^2) (V^2) \quad (13)$$

$E_{asy,av(max)}$, which is a state parameter, expresses the energy density of a capacitor at maximum voltage. However, $E_{asy,av(real)}$, which is a process parameter, expresses the energy density of a capacitor that can be stored/released during charge/discharge processes.

3.4. Power density of asymmetric capacitor

$$t_{asy} (\text{s}) = 1000 C_{asy,av} (\text{F g}^{-1}) \Delta V_{asy} (V) \times \left(\frac{1}{j_{ca} (\text{mA g}^{-1})} + \frac{1}{j_{ba} (\text{mA g}^{-1})} \right) \quad (14)$$

$$P_{asy,av(real)} (\text{W kg}^{-1}) = 3600 \frac{E_{asy,av(real)} (\text{Wh kg}^{-1})}{t_{asy} (\text{s})} \quad (15)$$

t_{asy} is the discharge time of a capacitor and $P_{asy,av(real)}$ is power density of a capacitor. Eq. (13) is substituted into Eq. (15):

$$P_{asy,av(real)} (\text{W kg}^{-1}) = \frac{1}{2} \frac{V_{asy,ds} + V_{asy,de}}{(1 + (1/x))} i_{ba} \quad (16)$$

4. Examples

From the above mathematical calculation, it is known that capacitor voltage, specific capacitance, energy density and power density are functions of mass ratio of two electrodes. Now take some examples from Table 1 to illuminate the influence of mass ratio on capacitor parameters. Meanwhile, organic LMO/AC system was assembled to prove the above results by comparing experimental results and calculation values.

4.1. Capacitor voltage

It can be known that when mass ratio x is smaller than capacity matching ratio x_{re} , capacitor voltage is proportional to mass ratio and when it equals to x_{re} , or is bigger than x_{re} , capacitor voltage reaches a peak value in Fig. 5(a). The capacitor voltages of two organic LMO/AC systems are different because charge cutoff potential of their AC negative electrode is not the same. For aqueous system in Fig. 5(a), its voltage is limited by decomposing potential of aqueous electrolyte. Capacitors consisted of battery-type and capacitor-type materials have similar voltage curves as functions of mass ratio x in Fig. 5(a) and (b). The organic AC/graphite system owns the highest voltage of all samples because its graphite negative electrode has the lowest potential, so its peak voltage reaches 4.35 V, which exceeds a Li-ion battery's work voltage.

For the system PFPT/LTO in Fig. 5(b), Pasquier and Laforgue [11] designed two mass ratio $x = 1/2.7$ and $1/3.9$ and the corresponding work voltage were 3.0 V and 2.75 V; the mass ratio $x = 1/2.7$ is bigger than capacity matching ratio x_{re} . According to Eq. (6), its work

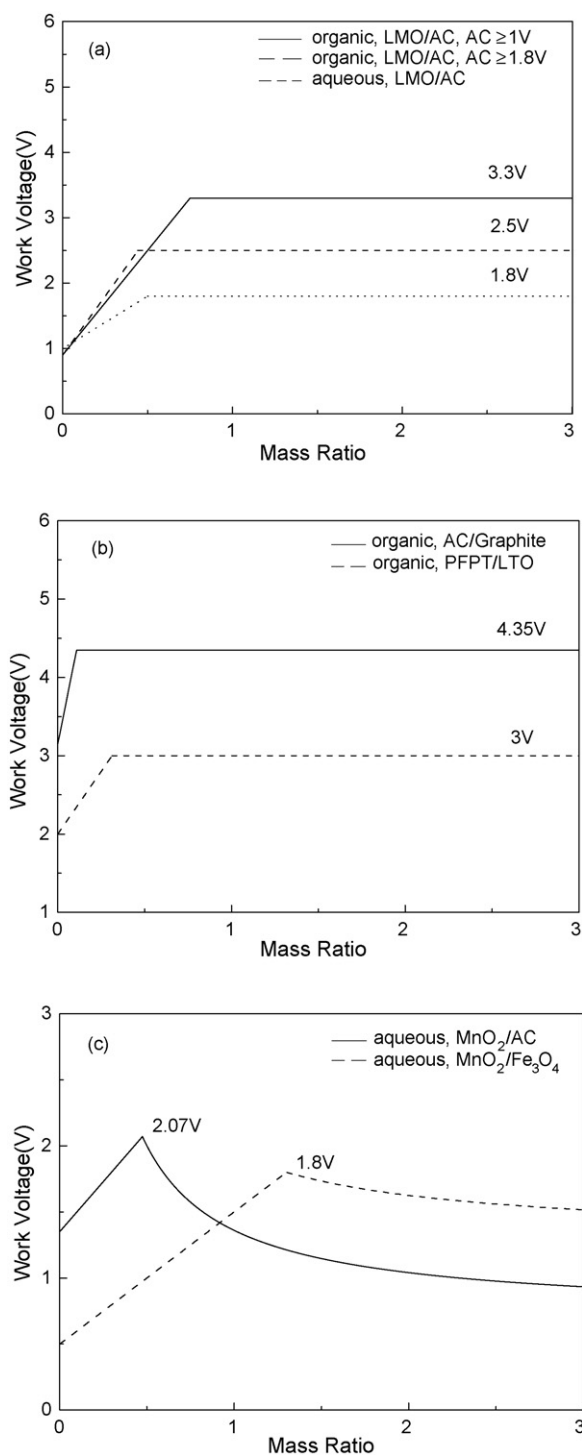


Fig. 5. Voltage curves of various types of asymmetric capacitors as a function of mass ratio, (a) battery-type (+)/capacitor-type (-), (b) capacitor-type (+)/battery-type (-), (c) capacitor-type (+)/capacitor-type (-).

voltage is 3 V, which accorded with actual value; the ratio $x = 1/3.9$ is smaller than capacity matching ratio x_{re} . According to Eq. (5), its work voltage is 2.82 V, which has the discrepancy of 0.07 V with experimental result 2.75 V, considering IR drop, charge/discharge platform and so on. It could be considered that the formula is in coincidence with experimental results.

Examples in Fig. 5(c) are aqueous systems; they both have lower work voltages. According to Eqs. (7) and (8), when mass ratio is smaller than capacity matching ratio x_{re} , capacitor voltage is in pro-

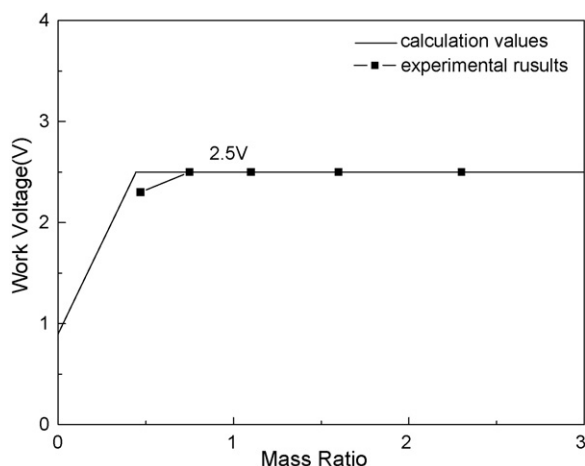


Fig. 6. Comparison of capacitor voltage of organic LMO/AC system between calculation and experimental values.

portion to the mass ratio; when the mass ratio is bigger than the capacity matching ratio x_{re} , capacitor voltage is in reverse proportion to mass ratio x . In Fig. 5(c), it can be seen that when mass ratio is equal to matching ratio x_{re} , capacitor voltage reaches a peak value.

With organic LMO/AC system assembled, and experimental results and calculation values compared, it can be seen that in Fig. 6 calculation values accord with experimental results. When mass ratio exceeds the capacity matching ratio x_{re} , capacitor voltage reaches the upper limit. AC electrode's potential could reach 0.8 V and even lower actually, but the cyclic life of capacitor would be shortened obviously. With the cyclic life of a capacitor considered, the potential of AC electrode is in fact limited to 1.8 V, thus resulting that capacitor voltage reaches 2.5 V.

4.2. Specific capacitance of asymmetric capacitor

From Fig. 7(a) and (b), the trend can be seen that the specific capacitance of a capacitor is in proportion to its capacitor-type electrode's specific capacitance and in inverse proportion to mass ratio. In Fig. 7(c), both the aqueous MnO_2/AC system and MnO_2/Fe_3O_4 system have a maximum specific capacitance ($42.4 F g^{-1}$ and $25.7 F g^{-1}$) and the corresponding mass ratio x is unequal to capacity matching ratio x_{re} . In other words, the specific capacitance of this type of capacitor will not reach the peak value which the system can achieve intrinsically at matching ratio x_{re} .

Homenko et al. [5] assembled the aqueous MnO_2/AC system on the basis of capacity matching. The specific capacitance was $35 F g^{-1}$ and the calculation result is $36.4 F g^{-1}$ on the basis of Eq. (10). With Coulombic efficiency and IR drop considered, it could be thought that the calculation values accurately accorded with experimental results. There is an optimal ratio which can be gained by Eq. (11) because both of its electrodes contribute the capacitance. Besides, capacitor voltage at the mass ratio can be gained by Eqs. (7) and (8).

In Fig. 8, it can be seen that the change tendency of specific capacitance of a capacitor with mass ratio, which was obtained in experiments, accords with calculation values. The bigger the comparative content of a capacitor-type electrode is, the higher the specific capacitance of a capacitor is. There is some gap between calculations and experiment results because the data cited from literatures to calculate were much bigger than those used in this experiment with LMO/AC system.

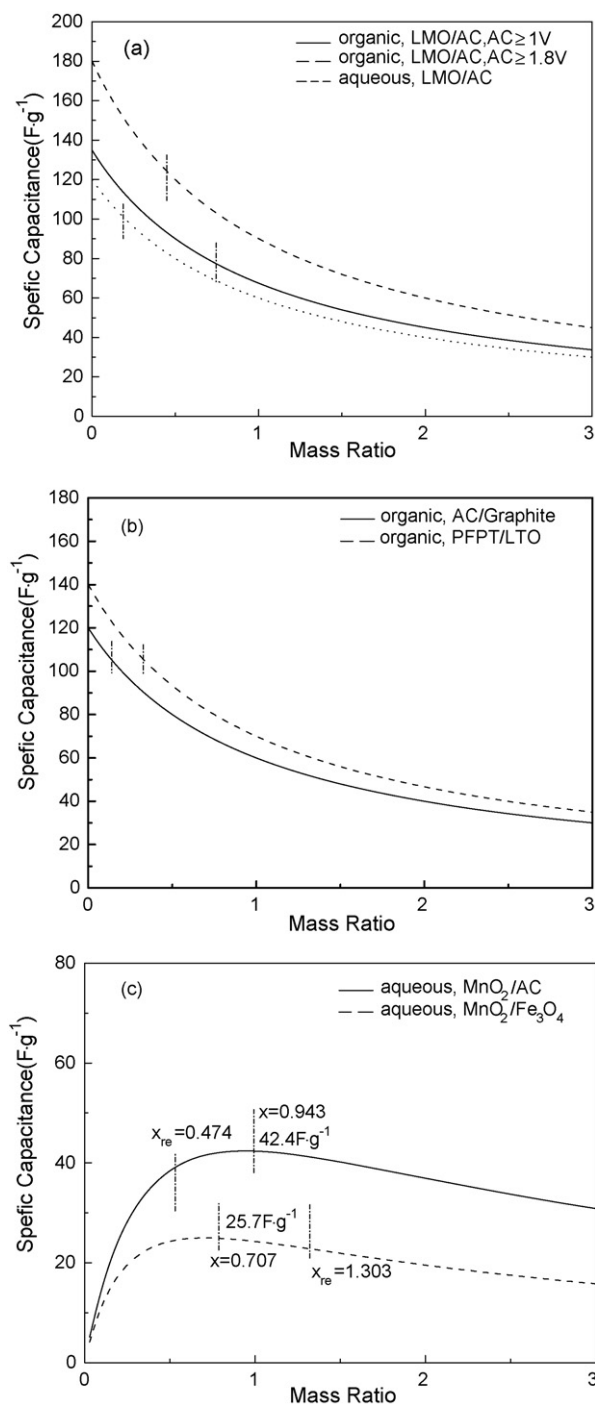


Fig. 7. Specific capacitance of various asymmetric capacitors, (a) battery-type (+)/capacitor-type (-); (b) capacitor-type (+)/battery-type (-); (c) capacitor-type (+)/capacitor-type (-).

4.3. Energy density of asymmetric capacitor

The real energy density $E_{asy,real}$ of organic LMO/AC system at capacity matching ratio x_{re} (AC potential $\geq 1V$ vs. Li^+/Li) is the biggest ($115.7 Wh kg^{-1}$) in Fig. 9(a) because, firstly, it is organic system and secondly, the potential of AC electrode is lower than those of other electrode materials; $E_{asy,real}$ and $E_{asy,max}$ are close to each other because the discharge ending voltage is closer to 0.0 V, e.g. 0.3 V (organic LMO/AC, AC potential $\geq 1V$), 0.5 V (organic LMO/AC, AC potential $\geq 1.8V$) and 0.8 V (aqueous, LMO/AC). So the electrode materials with wide ESWs, big gap between charge ending poten-

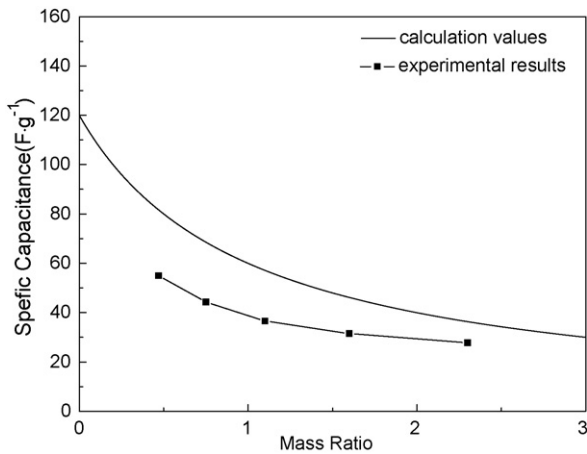


Fig. 8. Comparison of the specific capacitance of organic LMO/AC system between calculation and experiment values.

tials and small gap between discharge ending potentials should be selected when asymmetric capacitor was designed.

The positive electrode PFPT is pseudocapacitive polymer [11], which is similar to AC in the terms of capacitive behavior, but the negative electrode LTO's platform is much higher than graphite's platform. The voltage of organic AC/graphite system (4.35 V) is much higher than that of organic PFPT/LTO system (3 V). In Fig. 9(b), $E_{asy,max}$ is much higher than $E_{asy,real}$, such

as AC/graphite ($284.7 \text{ Wh kg}^{-1} > 126.4 \text{ Wh kg}^{-1}$) and PHPT/LTO ($133.4 \text{ Wh kg}^{-1} > 74.1 \text{ Wh kg}^{-1}$) because the big difference of discharge ending potentials such as 2.9 V (AC/graphite) and 1.9 V (PFPT/LTO) causes that much energy restored in capacitors can not be released.

The aqueous systems in Fig. 9(c) both have same discharge ending potentials between electrodes, so the cutoff voltage is 0 V; $E_{asy,real}$ is the same as $E_{asy,max}$, e.g. 22.3 Wh kg^{-1} (aqueous, MnO_2/AC) and 10.5 Wh kg^{-1} (aqueous, $\text{MnO}_2/\text{Fe}_3\text{O}_4$). Homenko et al. [5] assembled aqueous MnO_2/AC system on the basis of capacity matching and its energy density $E_{asy,real}$ was 21.0 Wh kg^{-1} while the calculation result is 22.39 Wh kg^{-1} on the basis of Eq. (13). With Coulombic efficiency and IR drop considered, it can be thought that calculation values accurately accords with experimental results.

It can be seen that the tendency of energy density of a capacitor with mass ratio in Fig. 10, which was obtained in experiments, accords with calculation values. The higher the comparative content of a capacitor-type electrode is at mass ratio of $x < x_{re}$, the lower the energy density of a capacitor is. However, it is opposite at mass ratio of $x > x_{re}$.

4.4. Power density of asymmetric capacitor

From Eq. (16), it is known that power density is in proportion to the current density and voltage. Here illustrated is the relationship between power density and mass ratio under the condition of small current density. From Fig. 11, it can be seen that the power density could reach the peak value at the capacity matching ratio x_{re} . The

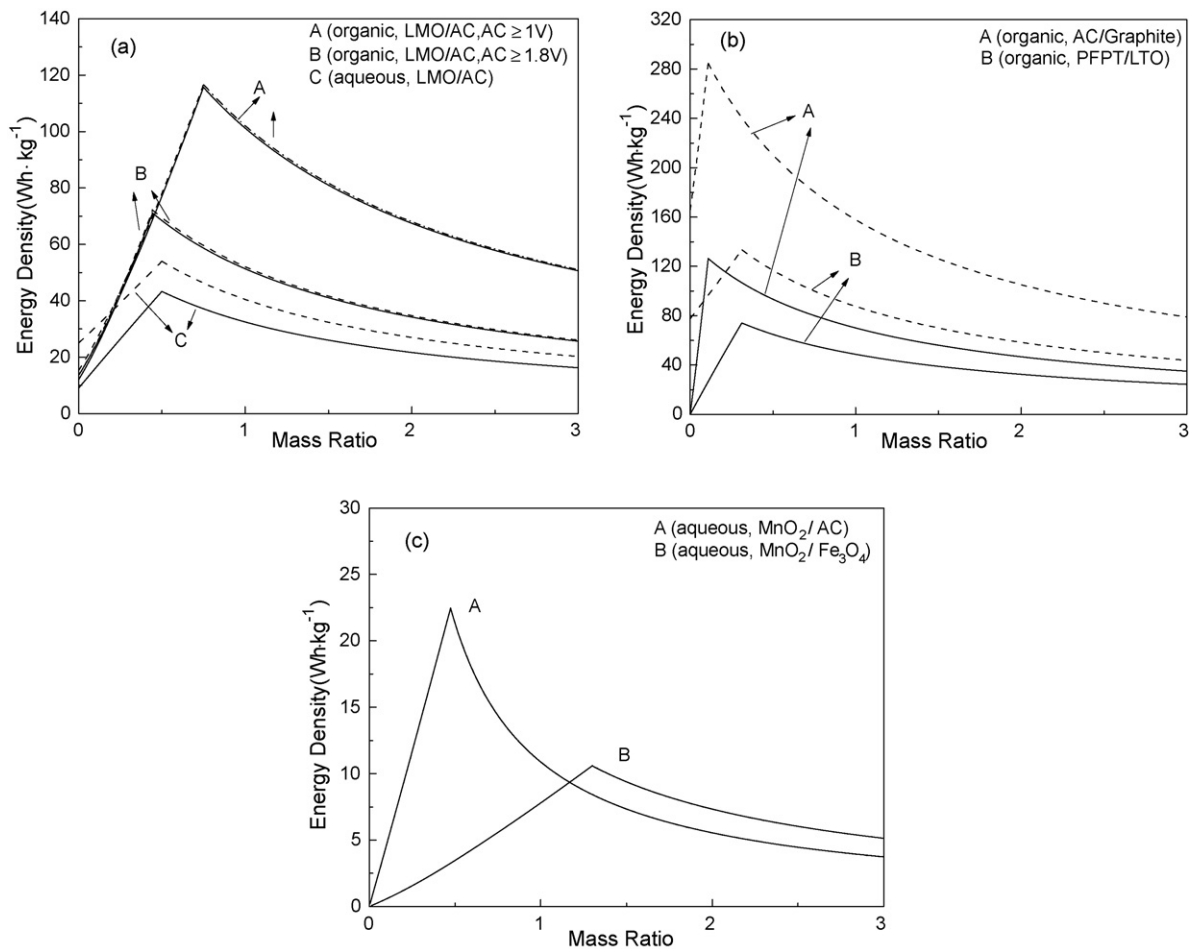


Fig. 9. Energy density of various asymmetric capacitors, (---) $E_{asy,max}$, (—) $E_{asy,real}$; (a) battery-type (+)/capacitor-type (-); (b) capacitor-type (+)/battery-type (-); (c) capacitor-type (+)/capacitor-type (-).

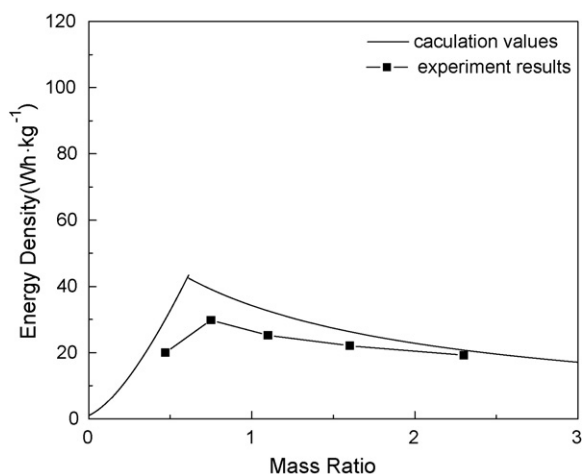


Fig. 10. Comparison between calculation and experiment values of the energy density of organic LMO/AC system.

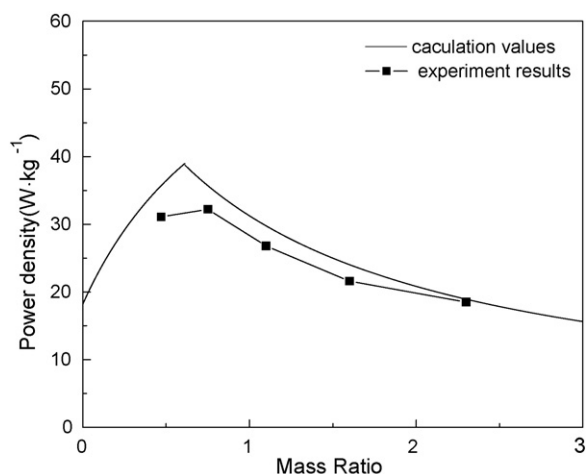


Fig. 12. Comparison between calculation and experiment values of power density.

better the rate capability of a battery-type electrode is, the bigger corresponding j_{ca} on the basis of capacity matching ratio x_{re} is, the higher the power density of a capacitor is. From Fig. 12, it can be seen that the tendency of power density of a capacitor with mass ratio, which was obtained in experiments, accords with calculation values. The higher the comparative content of a capacitor-type

electrode is at mass ratio of $x < x_{re}$, the lower the energy density of a capacitor is. However, it is opposite at mass ratio of $x > x_{re}$.

4.5. Influence of current density

In this paper, the matching mass ratio was investigated in view of potential matching in the above paragraphs. Here, the influence

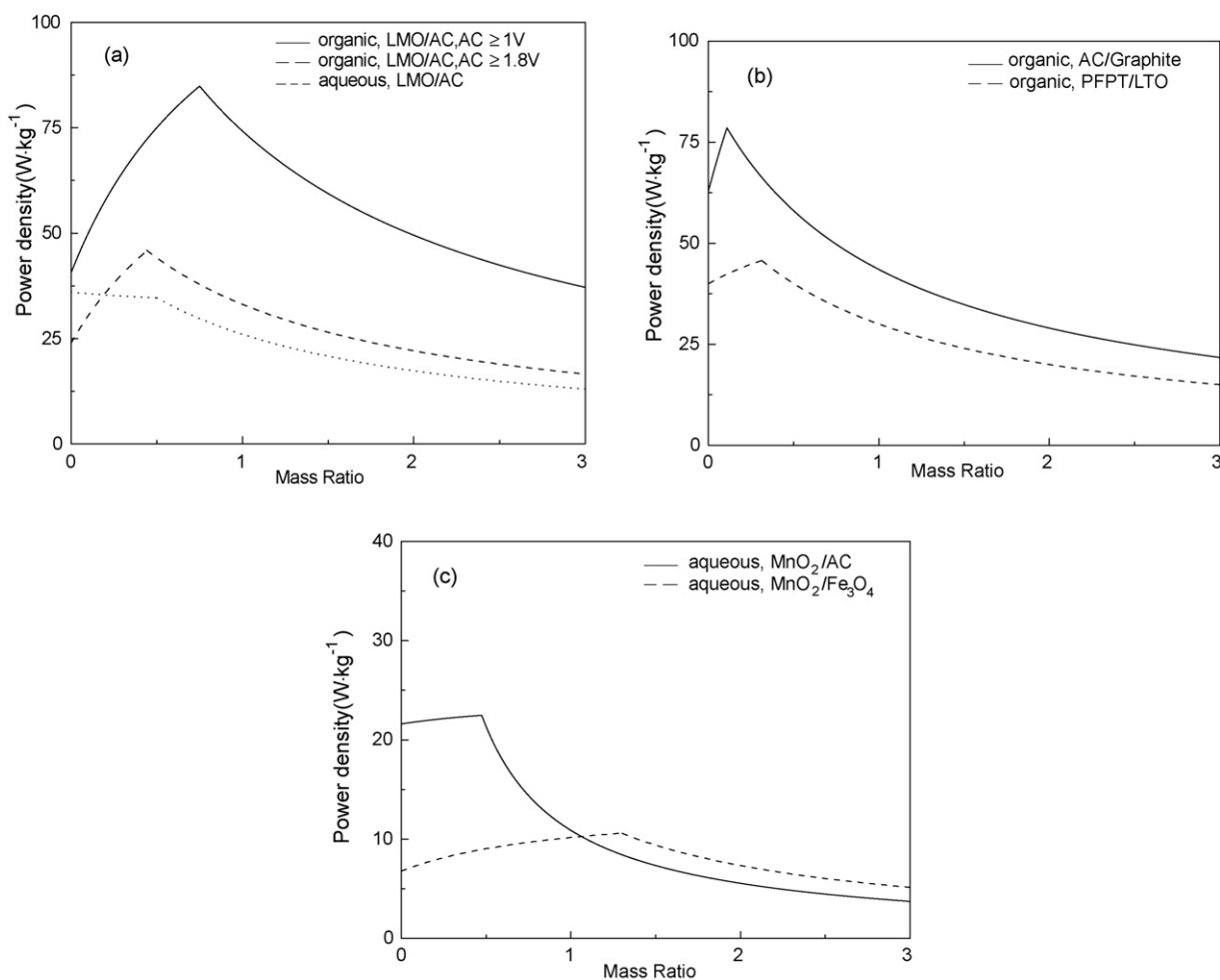


Fig. 11. Power density of various asymmetric capacitors, (a) battery-type (+)/capacitor-type (-); (b) capacitor-type (+)/battery-type (-); (c) capacitor-type (+)/capacitor-type (-).

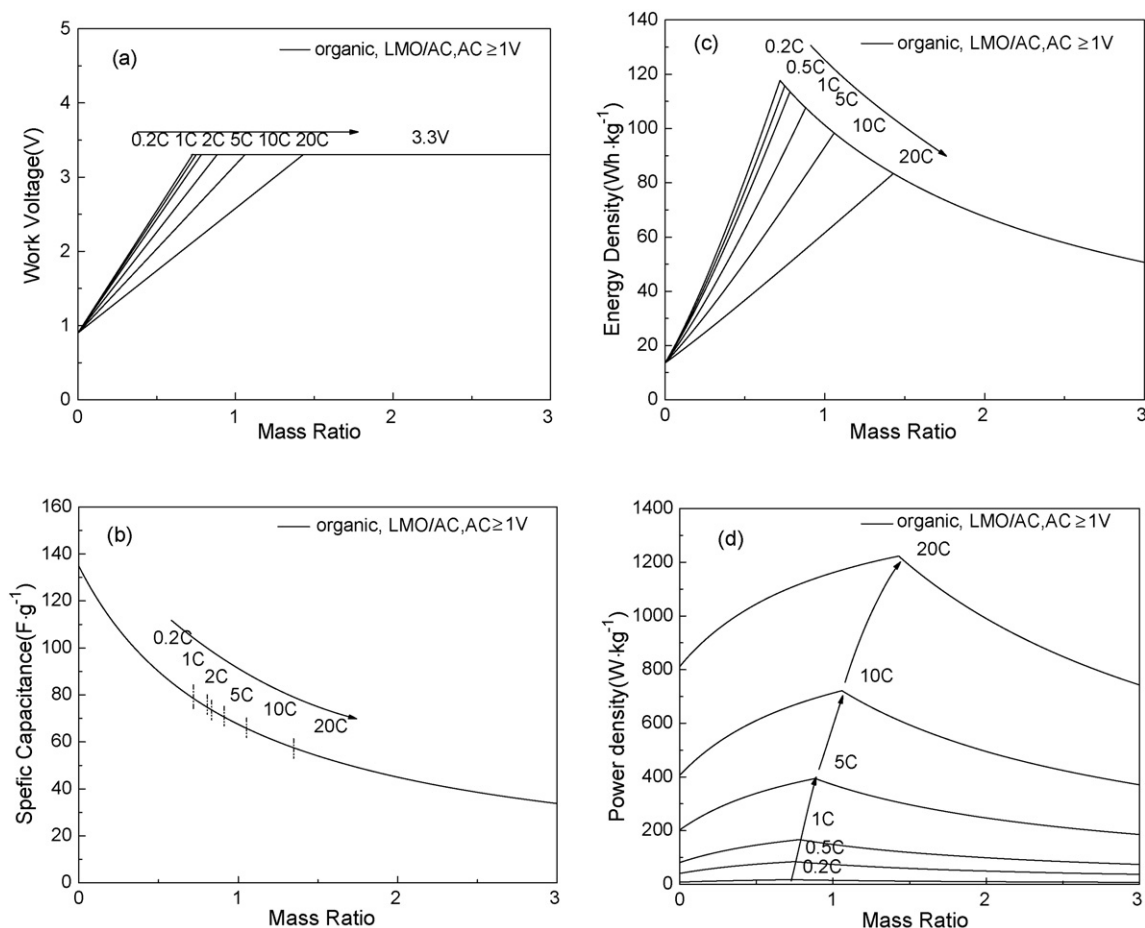


Fig. 13. Capacitor parameters of organic LMO/AC system as function of mass ratio, (a) work voltage; (b) specific capacitance; (c) energy density; (d) power density.

of current density is concretely discussed. When the current density gradually increases, the capacity of a battery-type electrode declines correspondingly. As a result, the capacity matching ratio x_{re} will increase according to Eq. (1).

Take organic LMO/AC system (AC electrode potential ≥ 1.0 V vs. Li^+/Li) for example. Park et al. [12] measured the specific capacities of LMO positive electrode from 0.1 C to 20 C. These capacity data of LMO with 20% conductive agent are adopted in this experiment to calculate and construct for showing the influence of current density on capacitor parameters.

It can be seen that the content of battery-type electrode increases in order to maintain the same work voltage when current rate increases from Fig. 13(a), and the work voltage is lower when the current density is bigger at the same mass ratio ($x < x_{re}$).

Fig. 13(b) shows that specific capacitance of organic LMO/AC system falls from 78.3 Fg^{-1} to 55.1 Fg^{-1} when current rate rises from 0.2 C to 20 C. The specific capacitance is in inverse proportion to mass ratio x by Eq. (14) and its mass ratio x correspondingly increases when current rate increases. So the specific capacitance declines with current density increasing.

The energy density is in proportion to the specific capacitance of organic LMO/AC system from the above formula. The energy density at 0.2 C reaches maximum (118.4 Wh kg^{-1}) in Fig. 13(c) and gradually declines when the discharge rate increases, to 84.2 Wh kg^{-1} at 20 C.

The power density is in proportion to current density of organic LMO/AC system, which is a function of matching ratio x . In Fig. 13(d), the mass ratio increases gradually with discharge rate increasing.

As a result the power density increases from 17.3 W kg^{-1} (0.2 C) to 1.23 kW kg^{-1} (20 C).

5. Conclusions

Mathematical analysis shows as long as the electrodes' potential range and rate capacities are fixed, the capacitor parameters (work voltage, specific capacitance, energy density and power density) at corresponding current rates can be attained.

For a battery-type|capacitor-type capacitor, its work voltage reaches a peak value when its mass ratio equals and exceeds the capacity matching ratio x_{re} ; its specific capacitance is in proportion to the specific capacitance of its capacitor-type electrode.

For a capacitor-type|capacitor-type capacitor, its work voltage reaches a peak value at its capacity matching ratio x_{re} ; when its mass ratio equals to $m_{ba}/m_{ca} = \sqrt{C_{ca}/C_{ba}}$, its specific capacitance can reach a maximum $\frac{1}{(1/\sqrt{C_{ca}}+1/\sqrt{C_{ba}})^2}$.

The energy density of a capacitor reaches a peak value at capacity matching ratio x_{re} as well as power density. The average energy density of a capacitor becomes higher at the lower discharge cutoff voltage.

For a battery-type|capacitor-type capacitor such as LMO/AC system, its capacity matching ratio and power density increase, while specific capacitance and energy density decline when charge/discharge current density increases. The electrochemical performances of this type of capacitor depend on the rate capacity of battery-type electrode.

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References

- [1] G. Glenn, Amatueei, J. Electrochem. Soc. 148 (8) (2001) A930–A939.
- [2] R. Kotz, M. Carlen, Electrochim. Acta 45 (2000) 2483–2498.
- [3] A.D. Pasquier, I. Plitz, S. Menocal, J. Power Sources 115 (2003) 171–178.
- [4] T. Brousseau, D. Bejälangerb, Electrochem. Solid-State Lett. 6 (11) (2003) A244–A248.
- [5] V.K. Homenko, E.R. Pinero, F. Beguin, J. Power Sources 153 (2006) 183–190.
- [6] Y.G. Wang, Y.Y. Xia, Electrochem. Commun. 7 (2005) 1138–1142.
- [7] G.X. Wang, B.L. Zhang, Z.L. Yu, et al., Solid State Ionics 176 (2005) 1169–1174.
- [8] A.D. Pasquier, A. Laforge, P. Simon, J. Power Sources 125 (2004) 95–102.
- [9] J.P. Zheng, J. Electrochem. Soc. 150 (4) (2003) A484–A492.
- [10] W.G. Pell, B.E. Conway, J. Power Sources 136 (2004) 334–345.
- [11] A.D. Pasquier, A. Laforge, J. Electrochem. Soc. 149 (3) (2004) A302–A306.
- [12] S.C. Park, Y.M. Kim, Y.M. Kang, J. Power Sources 103 (2004) 86–92.