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$Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$-based Electrodes for PHEV Applications: An Optimization

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Abstract $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathodes of approximately the same loading of active material with different amount of inactive materials were fabricated and calendared to different porosity. EV and HPPC tests revealed that $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode performance is a strong function of inactive material amount and porosity with respect to energy density, pulse power and cycling capability. $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ laminate containing 2% PVdF and 1.6% acetylene black at 30% porosity exhibits the best overall electrochemical properties including energy density, pulse power and cycleability. Combined with MCMB anode, the full cell delivers an energy density of 520 Wh/L which well exceeds the 40-mile energy-density goal announced by FreedomCar. The result illustrates that proper engineering of the cell, module, and pack design can well meet the PHEV 40-mile goal.

Key words: Lithium ion batteries, Hybrid electric vehicles, Inactive materials, Porosity

Introduction

Current investigations of lithium ion batteries are being focused on the application in plug-in hybrid electric vehicles (PHEV) because these batteries permit high energy and power density[1-3]. According to the PHEV goals recently announced by Freedomcar, the performance and life targets of lithium ion batteries are defined for two systems: One system must go 40 miles all electric with 5000 cycle life while the other one must go 10 miles all electric with the same cycle life. At 20 mph average driving speed, the 40 mile system should be optimized for a 2 hr discharge (C/2 rate) and the 10 mile system should

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be optimized for a ½ hr discharge (2C rate). Assuming 70% is available for all electric driving, 207 Wh/L and 121 Wh/L energy densities are required for the 40 mile system and 10 mile system, respectively.

How to develop a cathode to meet the aggressive PHEV goals is one of the critical issues for successful application of lithium ion batteries in electric vehicles. In the production of lithium ion battery cathode, there are several possible ways to improve the electrode's energy density for a given active material. One of the way, as we have reported, is to optimize the binder/carbon ratio as poly(vinylidene fluride) (PVDF) to conductive carbon (such as acetylene black) composition plays a significant role in the interfacial resistance and thus influences the energy density under high current density [4]. Another way is to reduce the inactive material amount to a minimum value. Inactive materials including PVDF binder and acetylene black are widely adopted in the production of electrodes to attain satisfactory mechanical and conductive properties of the laminates. With relatively lower density, the introduction of more inactive materials significantly decreases the volumetric ratio of active material in the electrode. Using minimum amount of inactive materials, without significantly decreasing the mechanical and conductive properties of the electrode, is an effective way to improve the volumetric energy density of the electrode. The third way is to reduce the porosity of the electrode by calendaring. Calendaring electrode is a critical step because the calendaring process can not only improve the adhesion between active materials and current collector, but also decrease electrode's thickness and change many of the physical parameters including the electrode density, ionic conductivity, and electronic conductivity, etc. Therefore, optimizing electrode porosity is also an important factor enhancing the electrode's energy density, pulse power, and even cycling capability[5.6].

$Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$, a layered transition metal oxide with hexagonal structure, is attracting significant interest in the recent years. Compared with other commonly used cathode materials in lithium ion batteries such as $LiCoO_2$, $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ shows large capacity, satisfactory cycling capability milder thermal stability at charged state, lower cost and less toxicity. This material is a promising cathode for lithium ion batteries for electric vehicle (EV) and hybrid electric vehicle (HEV) purpose[7,8]. The purpose of our study is to develop a $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode which can meet the 40-mile

energy-density goal through an investigation of the inactive material content and the electrode porosity.

Experimental

The active material for the cathode, $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ was supplied by Semi, USA. A slurry consisting different content of $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$, PVdF, acetylene black and large graphite (~ 6 microns diameter) was prepared by mixing in N-methyl-2-pyrrolidone (NMP). Four coated films on aluminium collector were prepared by doctor blade method. All the films were controlled to have approximately the same loading of active material (30mg/cm^2) to the best of our ability. The percentage of inactive materials, PVdF, acetylene black, and large graphite, was reduced from 8%, 6.4%, and 4% respectively to 8%, 6.4%, 0% and 4%, 3.2%, 0% and eventually to 2%, 1.6%, and 0%.

The free standing porosity of all the electrodes is around 45~50% calculated by hard sphere model simulation. Individual cathodes were cut from dried sheet and were then compressed to a desired thickness using a calendaring machine. The electrode porosities were adjusted from free standing to 40%, 30%, 20%, 10%, and 0%, respectively. A Hitach S-4700 scanning electron microscope operating at 200 kV was used to determine the changes of the electrode morphology with porosity.

Before using the electrodes, they are cut in small surfaces with an area of 1.26cm^2 and thoroughly dried for 16 h at 120 ^{o}C under vacuum. Coin cells were assembled in an argon-filled glove box (dew point $\leq$80 ^{o}C). Lithium foil and MCMB electrode were used as the counter electrode for the half cell and full cell, respectively. The separator employed was Celgard 2400. 1M $LiPF_6$/EC+DEC(1:1) was used as the electrolyte.

All cells were tested at 303K using Maccor battery cycler. Ten formation cycles at C/10 were used for all half cells and two cycles at C/24 for full cell. The discharge capacity in formation was also used to estimate the effective capacity of each cell and all subsequent cycles are based on this value. The battery energy was measured between 3.0 and 4.5 V for half cell and 3-4.4 V for full cell.

EV and hybrid pulse power characterization (HPPC) tests were performed following cell formation cycles. For the EV test, each cell was charged at C/10 and then fully discharged at rates of C/10, C/5, C/2, 1C, 2C, 5C, and 10C, respectively.. Following

these cycles, HEV pulse test were then performed. A sequence of 10s discharge (5C) and charge pulse (3.75C) test was performed at different depth of discharge (DOD).

The impedance spectra (100kHz to 10mHz, 5mV perturbation) of the half cells were recorded by using Sorlatron 1286 with three-electrode cells to remove the impedance of lithium. Prior to AC impedance measurements, the $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode was completely formed and held at a fixed potential of 4.2V for at least 1h to attain the condition of sufficiently low residual current.

Results and discussion

SEM images of the $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode containing 8% PVdF, 6.4% acetylene black and 4% large graphite at free standing (50%), 25%, and 0% porosities are shown in Fig. 1. It can be seen from Fig.1A that much space was occupied by inactive materials for this composite cathode at 50% porosity. The low volumetric ratio of active material must mean low energy density of the electrode. From this point of view, decrease the amount of inactive materials may considerably enhance the energy density of the electrode. With decreasing electrode porosity (see Fig.1B and Fig.1C), the electrode morphology was greatly changed. The distance between neighboring active particles was reduced due to the reduction of the electrode thickness. The porous inactive materials gathered together and even condensed. The binder/carbon composite, instead of shrinking uniformly, tends to fill the gaps within and even on the surface of the electrode. At 0% porosity, the electrode surface is seen covered mostly with binder/carbon composite and the active material particles are likely to be drowned in the binder/carbon matrix. We also observed some spaces in Fig. 1C with 0% porosity. This is because the porosity was calculated based on the assumption that no lateral expansion occurred during calendaring but actually it did.

Fig.2 shows the variation of the electrode thickness at different porosities with different inactive material contents in which the thickness of Al foil was not included. For $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode with approximately the same loading of active materials at free standing porosity, the thickness varies from 209 μm for the cathode containing 8% PVdF, 6.4% acetylene black and 4% graphite to 138 μm for the cathode containing 2% PVdF and 1.6% acetylene black. Similar trend is also observed for the

cathode at 30% and 0% porosities. This result clearly shows that removal of inactive material significantly reduces the electrode thickness. The reduction of electrode thickness should help to increase the electrode's energy density. Comparison of the cathode with the same inactive material amount at different porosities reveals that decrease the electrode porosity also considerably brought down the electrode's thickness. For the electrode containing 2% PVdF and 1.6% acetylene black, the thickness decreased from 112 μm at free standing (around 45% porosity) to 75 μm at 0% porosity.

Combination of decreasing inactive material amount and decreasing electrode porosity are even more significant in improving the volumetric ratio of active material in the electrode and thus enhance the electrode's energy density. With approximately the same loading of active material, The electrode thickness was decreased from 209 μm for the cathode containing 8% PVdF, 6.4% acetylene black and 4% graphite at 50% porosity to 75 μm for the cathode containing 2% PVdF and 1.6% acetylene black at 0% porosity. Around 64% space was saved as a result of different production technology of the laminate. Also, it is noted that the swell of all the laminates is no more than 2% in 1 M $LiPF_6$/EC+DEC (1:1) electrolyte.

Fig.3a to d shows the rate capability of the $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ electrode at different porosities with decreasing amounts of inactive materials. As we can see from Fig. 3 that most of the electrode with different amount of inactive materials and at different porosities can discharge at C/2 without significant discharge capacity loss. The discharge capacity sharply decreases when the current density is increased from C/2 to 1C and even higher. This result shows that the laminate is suitable for PHEV with C/2 discharge design. From comparison between Fig.3a, b, c and d, two points of conclusion can be derived. The first is that more porous electrodes perform better at moderate rates for the cathode with high level of inactive materials. For the electrode containing 8% PVdF, 6.4% acetylene black, 4% graphite and containing 8% PVdF, 6.4% acetylene black, 40% porosity exhibits the best discharge performance at around C/2 to C rate. With decreasing amount of inactive materials to 4% PVdF, 3.2% acetylene black and 2% PVdF, 1.6% acetylene black, the best high rate performance was obtained at around 20%, and 10% porosity, respectively. It should be noted that the rate performance of the cathode with 2% PVdF, 1.6% acetylene black at 10% porosity is well comparable with the electrode

containing 8% PVdF, 6.4% acetylene black at 40% porosity. The other conclusion draw from Fig.3 is that the lines become more tightly bundled as inactive material is removed. We believe this is directly related to the degree of electrode thickness changes.

To explain the satisfactory rate capability of the $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode containing minimum PVdF and acetelene black, electrochemical impedance spectroscopy (EIS) was carried out and presented in Fig.4. Impedance is a collective response of kinetic processes. All the diagrams show two semicircles. The high frequency limit refers to the bulk electrolyte resistance. The high-to-medium frequency semicircle is commonly attributed to the surface film on the compound[9,10]. Recently, some authors ascribe it to the bulk resistance at the active material particle/particle interface[11,12]. We would like to accept the later because it is more acceptable to explain our EIS results in this study. The semicircle in the middle frequency region is believed to be derived from the charge-transfer process at the electrolyte/electrode interface. The sloping line at low frequencies is attributed to the diffusion of lithium ions within the compound.

It is seen from Fig.4 that the bulk resistance of the $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode containing 2% PVdF and 1.6% acetelene black at 50% porosity is significantly high. The high bulk resistance of the electrode should be resulted from the shortage of inactive materials within the electrode. However, when the electrode porosity was decrease to 30%, the bulk resistance of the electrode sharply decreased. Continual decrease of the electrode porosity doesn't contribute to further considerable reduction of the bulk resistance. On the other hand, a slight increase of charge transfer resistance was observed when the electrode porosity decreased from 20% to 0%. 10% porosity of the electrode has the minimum impedance which is well in agreement with the best rate capability of the electrode in Fig.3d. This result indicates that the poor electrode conductivity aroused from the lack of inactive materials can be compensated by calendaring to a proper porosity.

Fig 5 is the Ragone plot showing the variations of the electrode energy density of the $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ electrode containing different amount of inactive materials and at different porosities with power density. The energy density and power density were calculated based on volume of cathode only. From comparison between Fig.5a, b, c and d, we see that the volumetric energy density and power density simultaneously improves

with decreasing inactive materials in the electrode. The improvement is, to a great extent, attributed to the reduction of the electrode thickness with removal of inactive materials. Also, the optimum porosity corresponding to the highest energy density at moderate rates decreases with removal of inactive materials. For the electrode containing 8% PVdF, 6.4% acetylene black, and 4% graphite, 30% porosity appears to be an optimum porosity because it exhibits the highest energy density at moderate C-rate. For the electrode containing 2% PVdF and 1.6% acetylene black, 0% porosity always shows the highest energy density. 30% optimum porosity designs appear to give way to much lower porosities as inactive material is removed.

Fig.5 illustrates that we can significantly improve the electrode's energy density by proper engineering of the laminate including decrease inactive material amount and calendaring. However, Energy density is just one factor that goes into the design of an electrode for PHEV goals, pulse power and cycling capability are two additional critical criteria that must be taken into consideration. To evaluate the pulse power and cycling performance of the $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode with different amounts of inactive materials at different porosity, we fabricated a matching counter electrode of meso-carbon micro-beads (MCMB) to test the cycling capability of our electrodes.

We present here the 40% depth of discharge (DOD) HPPC test results of the $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode containing 2% PVdF and 1.6% acetylene black at different porosities as shown in Fig.6. For the cell having $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode at 50% porosity at 40% DOD, the area specific impedance (ASI) is considerably high (around 43.8 Ohm-cm2). With decreasing electrode porosity from 50% to 30% porosity, the cell's ASI sharply decrease to around 27.9 Ohm-cm2. The significant ASI decrease is attributed to the closer contact between active particles and the filling of gaps between particles by the inactive materials. Continual decrease of the electrode porosity doesn't help to further reduce of the cell's ASI. This result we obtained from HPPC test well consists with the EIS measurements as shown in Fig.4.

Fig. 7 shows the cycling behavior of the $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode containing 2% PVdF and 1.6% acetylene black at different porosities combined with MCMB full cell. The cycling was conducted by charging at C/3 to 4.4V followed by trickle charging for 1h and then discharge to 3V at C/2. The poorest cycling performance of the cell with

$Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode at 50% porosity may be resulted from the high area specific resistance (see Fig. 5) because a cell with high ASI resists high rate cycling[13]. With decreasing ASI from 50% to 30% porosity, cycling capability of the cell greatly improved. However, cycling performance of the full cell becomes worse when the electrode porosity is lower than 20% which is possibly associated with the lack of electrolyte within the electrode. Here we obtained that $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode containing 2% PVdF and 1.6% acetylene black, 30% is the optimum porosity having the best cycling capability.

Taking energy density, pulse power and cycling capability into consideration, the $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode containing 2% PVdF and 1.6% acetylene black at 30% porosity seems to be the best one to meet the PHEV goals. The full cell energy density of all the cell components can be calculated based on the $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode containing 2% PVdF and 1.6% acetylene black at 30% porosity. The energy per area of the coin cell components we obtained in this study is 0.0160 Wh/cm^2. The thickness of the cathode, anode, separator, aluminium current collector, and copper current collector is 106, 132, 25, 25, and 28, respectively. Then, the Energy density of cell components is calculated to be 520 Wh/L. Even 70% is available for electric driving in PHEV, the cell can still deliver 360Wh/L! The practical operation value is significantly higher than the PHEV goal of 207 Wh/L energy density for 40 mile battery system at 70% DOD announced by FreedomCar.

Conclusion

The $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode performance is a strong function of inactive material amount and porosity with respect to energy density, pulse power and cycling capability. The electrode's energy density can be significantly improved through optimizing the inactive material amount and electrode porosity. With as little as 2% binder and 1.6% acetylene black and at 30% porosity, the $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode has high energy density, satisfactory low resistance, and good cycling capability. Combined with MCMB anode, the full cell has an energy density of 520 Wh/L. This value well meets the PHEV 40-mile goal. Considering that the anode we employed in this study is not optimized, even more exciting results may be obtained by further optimizing graphite anode in terms

of inactive materials and electrode porosity[14]. From this point of view, we conclude that proper engineering of the cell, module, and pack design can well meet the PHEV 40-mile goal!

Acknowledgments

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Figure captions

Fig.1 SEM images of the $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ cathode containing 8% PVdF, 6.4% acetylene black and 4% graphite at different porosities. A: 50%, B: 25%, C: 0%

Fig.2 Variation of the electrode thickness at different porosities with different inactive material contents

Fig.3 Rate capability of the Li[Ni1/3Mn1/3Co1/3]O2 electrode with different amounts of inactive materials. (The inactive materials PVdF, acetylene black and graphite are A: 8%, 6.4%, 4%; B: 8%, 6.4%, 0%; C: 4%, 3.2%, 0% and D: 2%, 1.6%, 0%, respectively.)

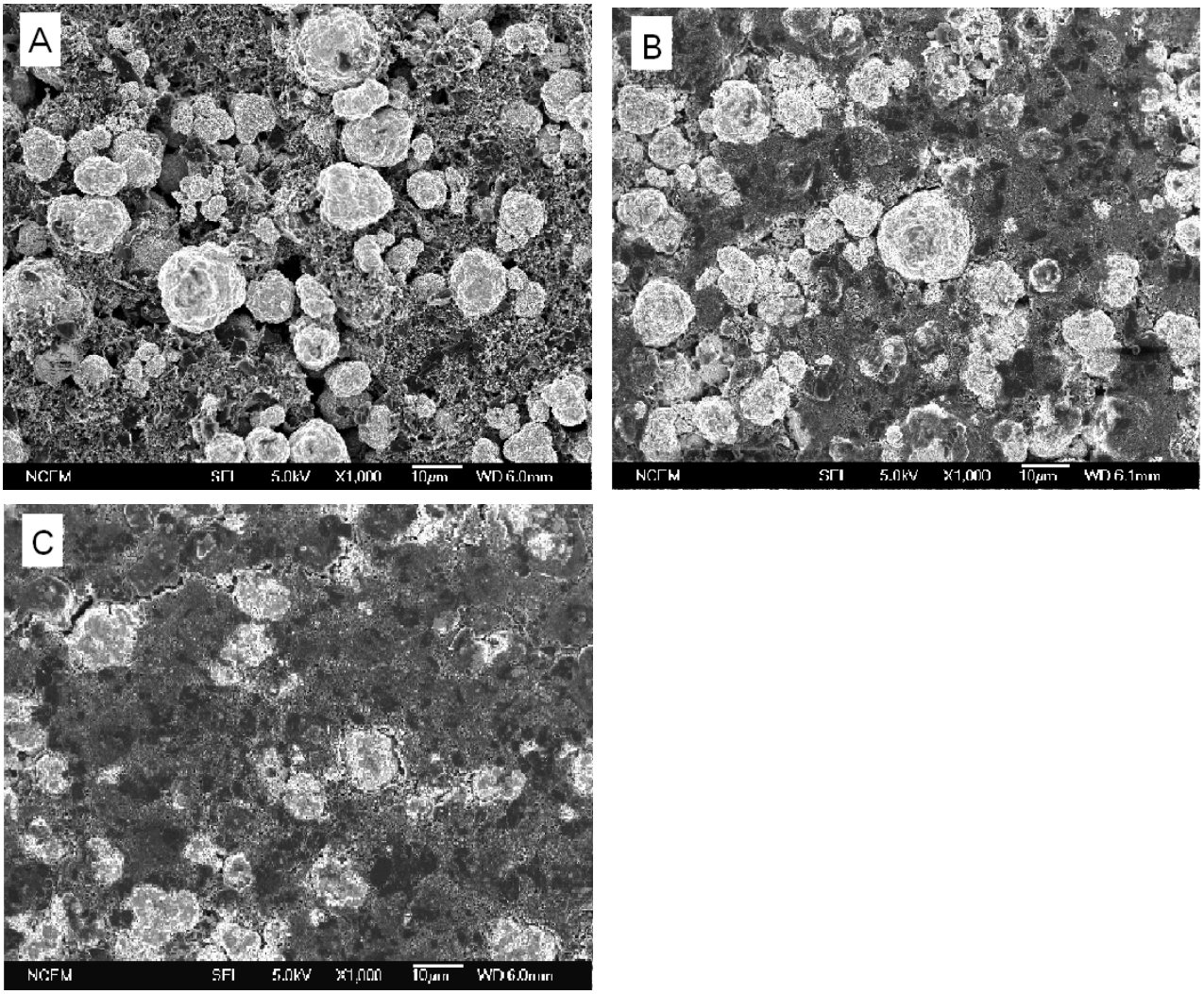
Fig.4 Nyquist plots of the Li[Ni1/3Mn1/3Co1/3]O2 electrode containing 2% PVDF 1.6% carbon at 4.2 V after 10 formation cycles

Fig 5 The Ragone plot of the $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ electrode containing different amount of inactive materials at different porosities with power density. (The inactive materials PVdF, acetylene black and graphite are A: 8%, 6.4%, 4%; B: 8%, 6.4%, 0%; C: 4%, 3.2%, 0% and D: 2%, 1.6%, 0%, respectively.)

Fig.6 Variation of area specific impedance (ASI) of the Li[Ni1/3Mn1/3Co1/3]O2 cathode containing 2% PVdF and 1.6% acetylene black at 40% DOD with electrode porosities

Fig.7 Cycling behavior of the Li[Ni1/3Mn1/3Co1/3]O2 cathode containing 2% PVdF and 1.6% acetylene black combined with MCMB full cell.

Fig.1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NCFM SEI 5.0kV X1,000 10μm WD 6.0mm
B
NCFM SEI 5.0kV X1,000 10μm WD 6.1mm
C
NCFM SEI 5.0kV X1,000 10μm WD 6.0mm

Fig.2

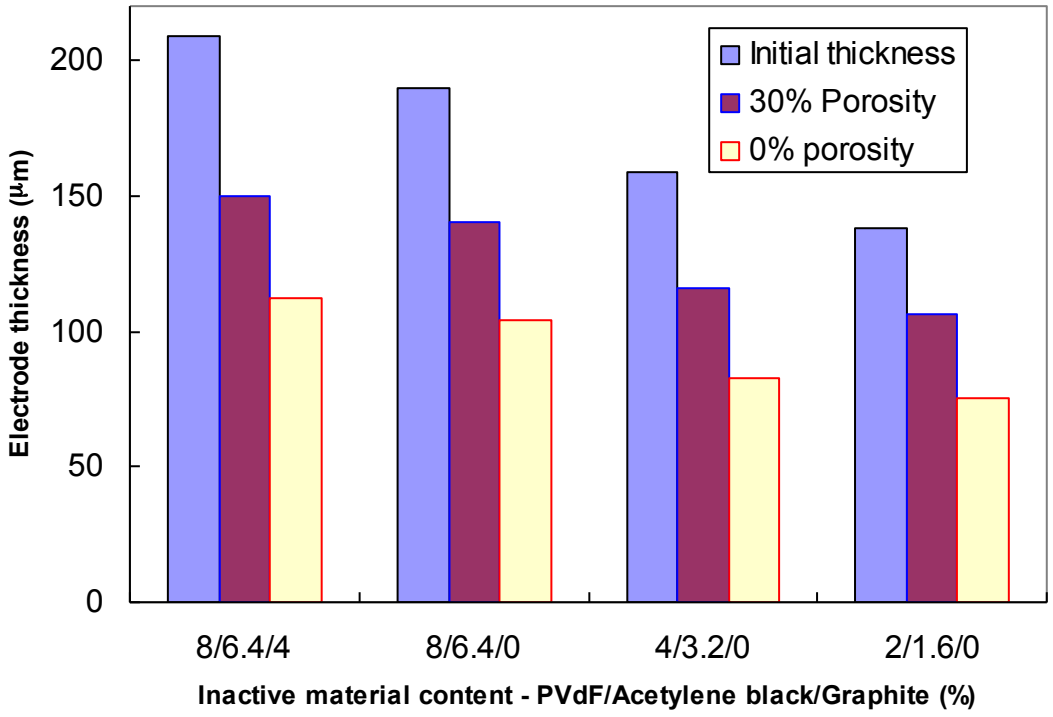
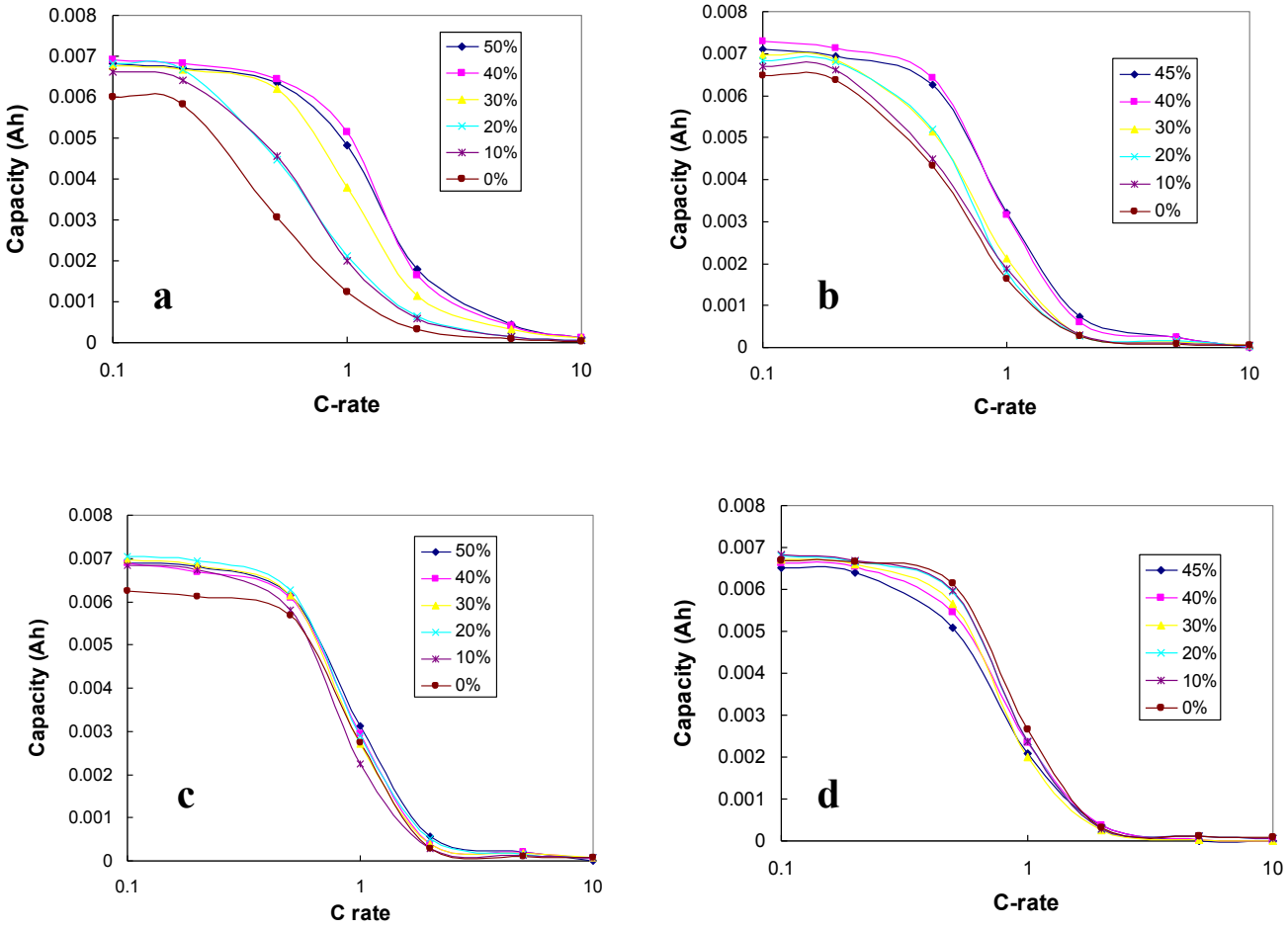

Initial thickness
30% Porosity
0% porosity
Electrode thickness (µm)
200
150
100
50
0
8/6.4/4
8/6.4/0
4/3.2/0
2/1.6/0
Inactive material content - PVdF/Acetylene black/Graphite (%)

Fig.3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Capacity (Ah)
C-rate
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0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0.1
1
10
50%
40%
30%
20%
10%
0%
b
45%
40%
30%
20%
10%
0%
c
C rate
d

Fig.4

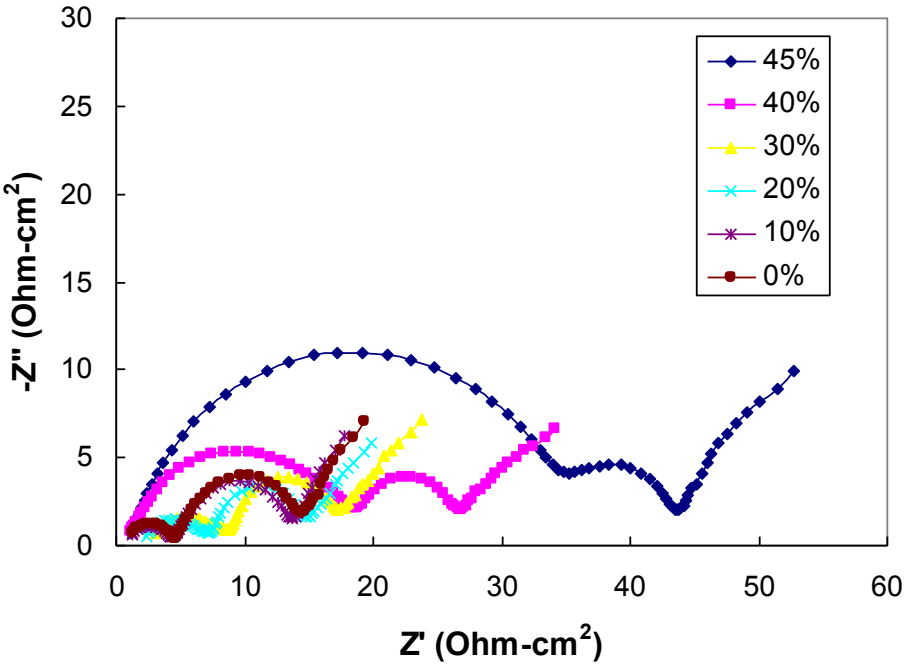
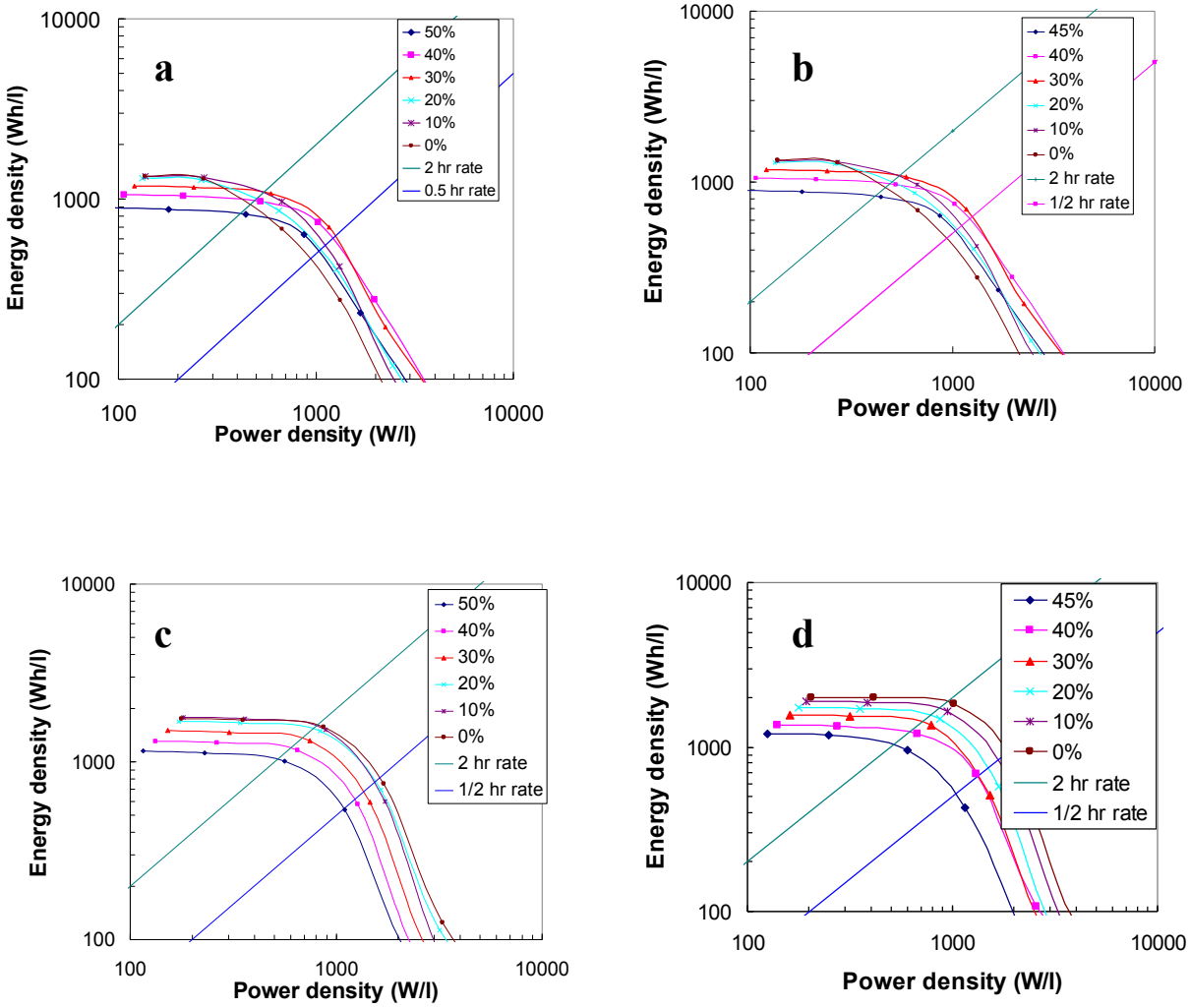

45%
40%
30%
20%
10%
0%
-Z'' (Ohm-cm2)
Z' (Ohm-cm2)
0
5
10
15
20
25
30
0
10
20
30
40
50
60

Fig.5


a
b
c
d
Energy density (Wh/l)
Power density (W/l)
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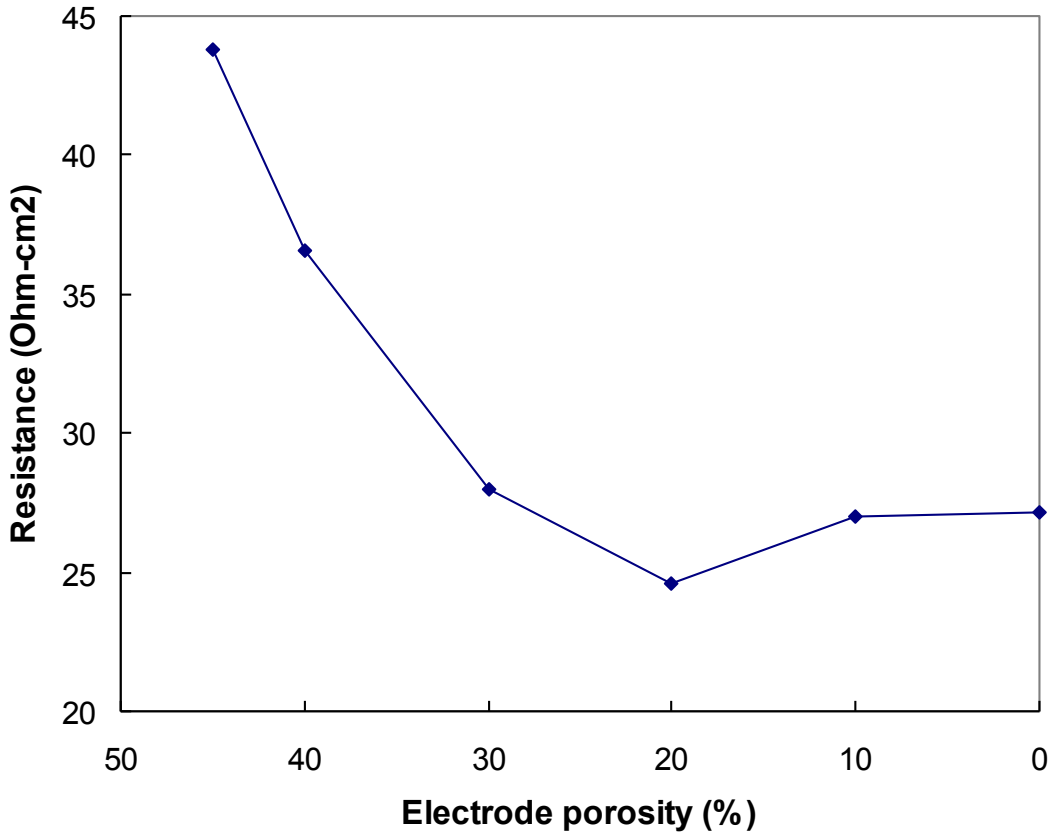
1000
100
50%
45%
40%
30%
20%
10%
0%
2 hr rate
0.5 hr rate
1/2 hr rate

Fig.6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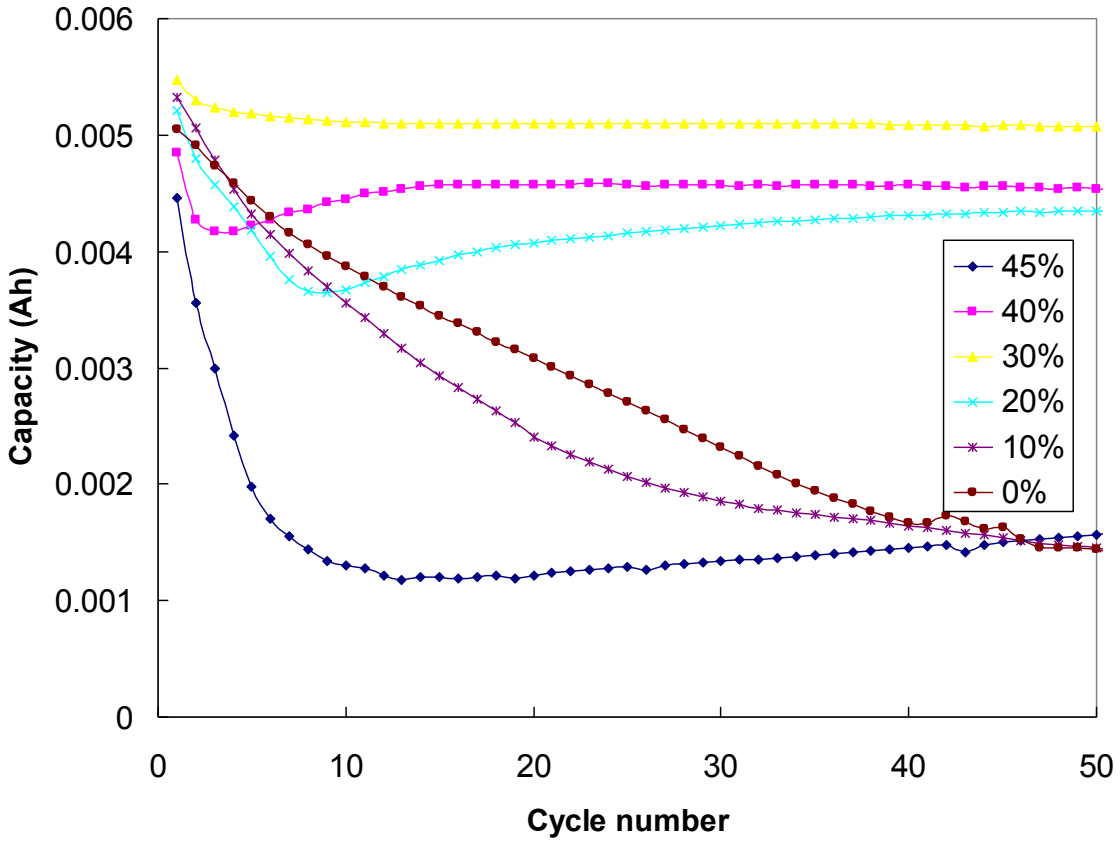
40
35
30
25
20
Resistance (Ohm-cm2)
50
40
30
20
10
0
Electrode porosity (%)

Fig.7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0
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20
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50
Cycle number
45%
40%
30%
20%
10%
0%