

Short communication

Capacity and cycle performance of a lithium-ion polymer battery using commercially available LiNiCoO_2

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Abstract

Commercially available lithium–nickel–cobalt oxide ($\text{LiNi}_{0.82}\text{Co}_{0.18}\text{O}_2$) issued a high-capacity cathode material in the fabrication of a bi-cell type of lithium-ion polymer battery (LIPB) following the Bellcore scheme. The capacity and cycle performance of the battery is evaluated. An ethylene carbonate (EC)-based electrolyte mixed with dimethyl carbonate (DMC) or ethyl methyl carbonate (EMC) is employed as a means to increase the utilization of cathode active material. $\text{LiNi}_{0.82}\text{Co}_{0.18}\text{O}_2$ displays a higher initial discharge capacity ($\sim 180 \text{ mAh g}^{-1}$) than conventional LiCoO_2 . As a result, both capacity and cycle performance are improved when using an EMC-containing electrolyte solution. In particular, the high-rate capability is enhanced, e.g. the discharge capacity at the 2C rate reaches about 70% of that at the 0.2C rate. All the improved performance characteristics are probably due to the EMC-containing electrolyte solution causing a trans-esterification reaction associated with an equilibrium mixture of EMC, DMC and diethyl carbonate (DEC).

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1. Introduction

Lithium-ion polymer batteries (LIPBs) feature both dimension and shape flexibility as well as improved safety and therefore very promising power sources for portable electronics such as cellular phones, personal digital assistants and laptop computers. In contrast to lithium-ion batteries using porous separators and liquid electrolytes LIPBs are mainly specified by adopting polymer electrolyte membranes that entrap the electrolyte solution. Various types of commercial LIPB products are now available on the market. Of these, stacked bi-cell laminates which are prepared via plasticization, extraction and activation processes best known as the Bellcore process (now licensed by Telcordia Technologies) [1].

The core technologies of the Bellcore process, as defined by a series of patents [2], are as follows: (i) lamination of positive electrode (cathode; lithium-intercalation oxide material) with aluminum mesh; (ii) lamination of negative electrode (anode; graphite or carbon material) with copper mesh; (iii) poly(vinylidene fluoride-co-hexafluoropropylene)

(PVdF-HFP)-based polymer electrolyte filled with fumed silica and simultaneously plasticized by dibutyl phthalate (DBP); (iv) lamination of ‘cathode/(polymer electrolyte)/anode/(polymer electrolyte)/cathode’ to give a bi-cell; (v) extraction of plasticizer by diethyl ether or methanol; (vi) activation of bi-cell with electrolyte solution under moisture-free conditions; (vii) tight packaging within polyester-aluminum pouch. An important feature of this technology is that all these steps can be organized into a continuous line of production. The LIPB produced by the Bellcore process, under the PLiON™ trade mark [3], has many advantages such as inherent design flexibility, long-cycle life and improved safety.

The consumer demand for high-capacity batteries calls for cathode materials that have higher capacity than conventional LiCoO_2 . Various active materials for high-voltage ($\sim 4 \text{ V}$ class) cathodes have been developed for higher capacity but, to date, have failed to replace LiCoO_2 . Recently, however, appreciable amounts of lithium–nickel–cobalt oxides (LiNiCoO_2) for practical LIPB production have become available commercially from several Japanese companies [4]. LIPBs using commercial LiNiCoO_2 , particularly $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, have been studied for several applications [5–7]. The LiNiCoO_2 is expected to exhibit better rate

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capability and higher capacity than LiCoO_2 (following the propensity of to give high-capacity), as well as better thermal stability than LiNiO_2 (following the tendency for LiCoO_2 to show good thermal stability).

As mentioned above, LIPBs prepared from LiNiCoO_2 via the Bellcore process may be expected to show superior capacity and cycling behavior. These improvements may, however, depend strongly on the electrolyte component used, particularly during the first charging step. For instance, high-voltage charging up to 4.1 and 4.2 V appears to cause a significant problem at cathode potentials of 4.15 and 4.26 V versus Li/Li^+ , respectively, by the degradation of electrolyte components when the anode uses carbon materials [8]. It is therefore important to choose an electrolyte component that is stable at high-voltages in order to increase the degree of utilization of the cathode active materials (or to charge up to high-voltages such as 4.2 or 4.3 V). In the present work, two ethylene carbonate (EC)-based electrolyte solution systems are examined as recommended by Yoshida et al. [9], namely 1 M LiPF_6 dissolved in a mixture of EC/dimethyl carbonate (DMC) or EC/ethyl methyl carbonate (EMC). The studies are preformed prototype LIPBs that use commercial LiNiCoO_2 and are prepared via a slightly modified Bellcore process.

2. Experimental

2.1. Materials

The commercially available $\text{LiNi}_{0.82}\text{Co}_{0.18}\text{O}_2$ cathode material was NC-118 powder (Seimi Chemical Co.) with a specific surface-area of $0.69 \text{ m}^2 \text{ g}^{-1}$ and average particle diameter of $8.3 \mu\text{m}$. The anode material was meso-carbon microbead powder (MCMB 10–28, Osaka Gas Co.) graphitized at 2800°C to give an average particle diameter of $10 \mu\text{m}$. Carbon black material (Super P, MMM Carbon Co.) was also used as a conductive agent in preparing the slurries for the cathode and the anode. Poly(vinylidene fluoride-co-hexafluoropropylene), used as both a binder material of electrodes and a matrix material of polymer electrolyte, was KynarFlex[®] 2801 powder (Atofina Chemicals Co.) which contains 12 mol% hexafluoropropylene. The fumed silica was a disilazane-treated SiO_2 powder (Cab-O-Sil[®] TS-530, Cabot Co.). Prior to make slurries, all the powder samples were dried at 100°C for at least 12 h in a vacuum oven.

The liquid chemicals employed were acetone (high purity grade, Aldrich) as a solvent, DBP (Showa Chemical Co.) as a plasticizer, diethyl ether and methanol (Aldrich) as extraction agents, and electrolyte solutions of 1 M LiPF_6 (EC:DMC, 2:1 mol) (lithium battery grade, Mitsubishi Chemicals Co.). Aluminum (for cathode) and copper (for anode) meshes served as current-collectors and were supplied by Exmet Corp. They were designated as 4/5 which signifies diamond dimensions of 1.9 mm (long way) and

0.82–9.94 mm (short way) and the thickness of about $50 \mu\text{m}$. The LIPB was packaged in a polyester coated aluminum pouch (five layers laminated).

2.2. Fabrication

Positive (cathode) and negative (anode) electrodes were prepared by mixing the constituents (active material, conductive agent, binder, and solvent) to give slurries that were coated on a substrate film (i.e. transparent poly(ethylene terephthalate) film, $10 \mu\text{m}$ thick). The substrate film was temporarily used to give electrode sheets after peeling. The slurry for the polymer electrolyte film was also prepared by mixing the constituents (polymer, plasticizer, filler, and solvent) and then coating on a substrate film. The constituents and their compositions in slurries are summarized in Table 1. The mixing process was performed using a planetary mixer equipped with double-twisted blades and, consequently, with a homogenizer equipped with a high-speed impeller. The coating process was also carried out with a precision coating machine (Hirano Tecseed Co.) that had two 1.5 m long drying chambers to evaporate the solvent component by blowing hot air (30°C). The coating machine offers the advantage of producing, with high-speed, massive amounts of sheets of electrodes and polymer film of uniform thickness. After peeling from the substrate film, the average thickness of the electrodes and the polymer film was found to be about $85 \mu\text{m}$ for the cathode, $100 \mu\text{m}$ for the anode, and $40 \mu\text{m}$ for the polymer film. The weights of cathode and the anode-sheets ($3 \text{ cm} \times 6 \text{ cm}$) were averaged over 100 sheets as 0.311 ± 0.01 and $0.292 \pm 0.008 \text{ g}$, respectively.

Prior to fabrication of the bi-cell, aluminum and copper meshes, each of size $2.9 \text{ cm} \times 5.9 \text{ cm}$ with a tab (width 1 cm, length 2 cm) were prepared as current-collectors for each electrode. As shown in Fig. 1 the cathode was made by lamination of a cathode-sheet ($3 \text{ cm} \times 6 \text{ cm}$)/Al mesh/cathode-sheet ($3 \text{ cm} \times 6 \text{ cm}$) assembly at 120°C using a double-roll press with the gap of $150 \mu\text{m}$ at an applied

Table 1
Constituents and compositions used in making electrodes and polymer film

	Composition (wt.%)		
	Cathode	Anode	Polymer film
$\text{LiNi}_{0.82}\text{Co}_{0.18}\text{O}_2$	70	–	–
MCMB 10–28	–	70	–
Super P	6	3	–
PVdF-HFP	9	9	30
DBP	15	18	40
SiO_2	–	–	30
NV ^a	40	50	30
Sheet thickness (μm) ^b	85	100	40
Area density (mg cm^{-2}) ^a	17.3	16.2	–

^a Weight percentage of non-volatile components in slurry, calculated as (weight of total constituents except solvent \times 100)/weight of slurry.

^b Average value for at least three measurement.

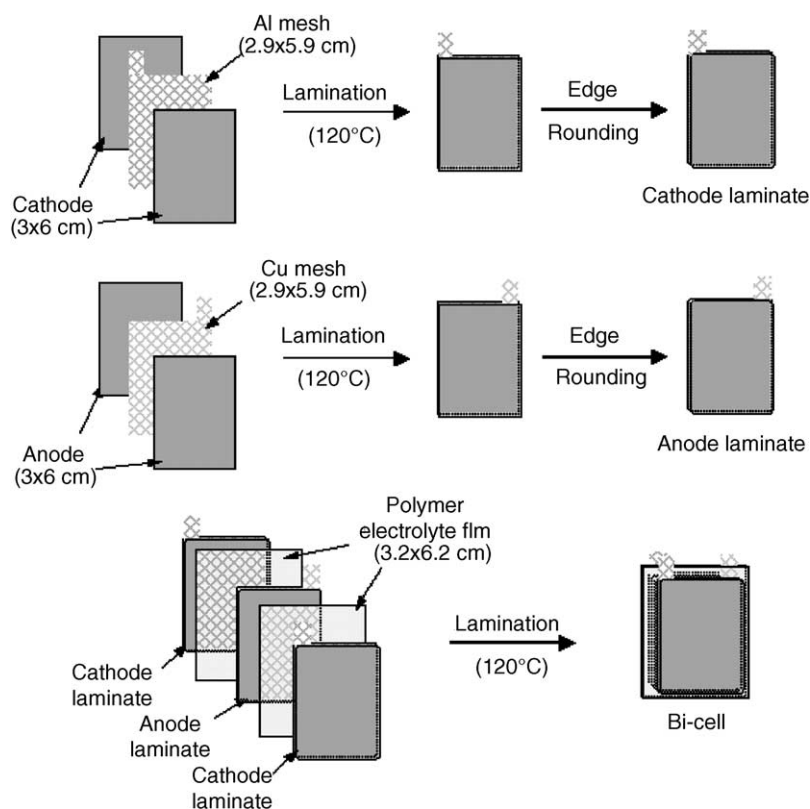


Fig. 1. Schematic illustration of preparation of cathode and anode laminates and bi-cell.

line-pressure of about 50 kg cm^{-1} . Three corners of the cathode laminate were cut to prohibit the penetration of sharp corners of electrodes into the polymer electrolyte film during further lamination to yield the bi-cell. The anode laminate was prepared in the same manner as the cathode laminate, but copper mesh was used instead of aluminum mesh. Two sheets of polymer electrolyte film ($3.2 \text{ cm} \times 6.2 \text{ cm}$) with two cathode laminates and one anode laminate were combined to make the bi-cell, as shown in Fig. 1. The function of the DBP plasticizer is to form micropores in the electrodes and the polymer film, and to enhance the adhesion between them during bi-cell lamination. That is, the DBP helps the free-volume expansion and then the affinity increases of PVdF-HFP chains between the electrodes and the polymer film during bi-cell lamination.

The amounts of active materials contained in a bi-cell were calculated as follows: for $\text{LiNi}_{0.82}\text{Co}_{0.18}\text{O}_2$ ($0.311 \text{ g/cathode-sheet}$) ($4 \text{ cathode-sheets/bi-cell}$) (0.7) = 0.871 g and for MCMB 10–28 ($0.292 \text{ g/anode-sheet}$) ($2 \text{ anode-sheets/bi-cell}$) (0.7) = 0.409 g . The factor 0.7 refers to the weight fraction of active material in each electrode. A rough estimation of the capacity balance between the cathode and the anode may be possible in that the charge capacity of MCMB 10–28 (ca. 300 mAh g^{-1}) $\times 0.409 \text{ g}$ = 123 mAh) corresponds to the specific discharge capacity of $\text{LiNi}_{0.82}\text{Co}_{0.18}\text{O}_2$ ($123 \text{ mAh}/0.871 \text{ g}$ = 141 mAh g^{-1}).

Precise and accurate estimation for capacity balance should be completed after obtaining the formation data of LIPB.

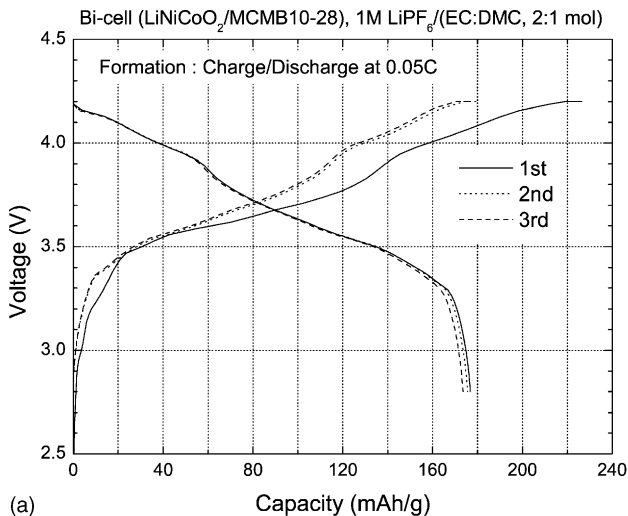
Aluminum and nickel leads (width 0.8 cm , length 5 cm , thickness $100 \mu\text{m}$) were welded to the aluminum and copper tabs in the bi-cell using an ultrasonic welding machine. To extract the DBP within the electrodes and polymer electrolyte film, the bi-cell was immersed in a bath which contained diethyl ether for 0.5 h , re-immersed twice in methanol for 0.5 h with ultrasonic vibration, and finally dried in a vacuum oven at 80°C for 12 h . Measuring and comparing the weights of the bi-cell before and after the extraction showed that the weight difference was almost equal to the total amount of DBP added initially.

The bi-cell was taken to a dry room with an ultra-low humidity condition (moisture content less than 0.1 ppm), and then immersed in a bath which contained the electrolyte solution for 24 h to absorb sufficient electrolyte into the micropores formed by the extraction of DBP. The wetted bi-cell was then patted lightly with filter papers several times to remove surface liquid, and inserted into the polyester-aluminum pouch. Tight packaging was completed by melt-pressing at 150°C the tab-side edge of the pouch under vacuum conditions. The open circuit voltage and bulk resistance of the LIPB were $\sim 30 \text{ mV}$ and $\sim 50 \text{ m}\Omega$, respectively. Many bi-cell LIPBs with different electrolyte solutions were prepared for capacity and cycle tests.

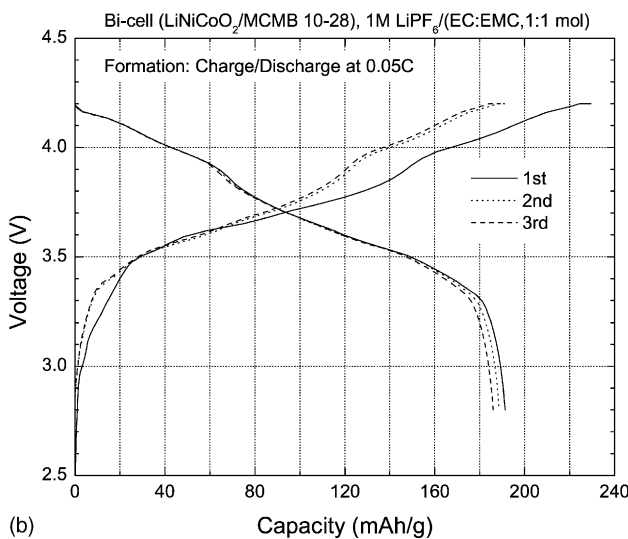
2.3. Performance tests

To attain the full capacity of $\text{LiNi}_{0.82}\text{Co}_{0.18}\text{O}_2$, the LIPB should pass through a formation step, i.e. repeated charge–discharge at a very low C rate. Temporarily setting the specific discharge capacity of $\text{LiNi}_{0.82}\text{Co}_{0.18}\text{O}_2$ at 150 mAh g^{-1} , i.e. slightly higher than 140 mAh g^{-1} from the above simple estimation, the current at the 1.0C rate corresponds to $(150 \text{ mAh g}^{-1}) (0.871 \text{ g})/\text{h} = 130 \text{ mA}$. To form the LIPB, very slow charge–discharge was performed three times as follows: constant-current charge at 0.05C rate (6.5 mA) up to 4.2 V followed by constant-voltage charge for 2 h and rest for 20 min; constant-current discharge at 0.05C rate (6.5 mA) down to 2.8 V and rest for 20 min. All tests were performed using a 32-channel cycler (Maccor Co.).

After formation, the capacity and cycle performance were measured over more than 200 cycles via the following schedule: constant-current charge at 0.2C rate (26 mA) up to 4.2 V



(a)



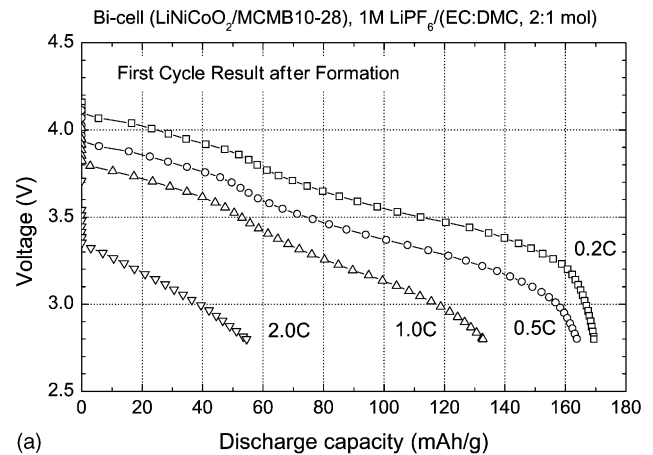
(b)

Fig. 2. Charge–discharge curves obtained from formation step; charge–discharge repeated three times at 0.05C rate.

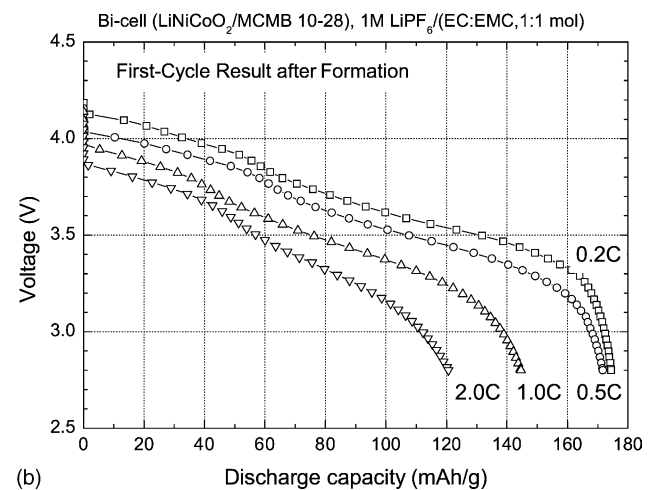
followed by constant-voltage charge for 2 h; constant-current discharge at various C rates (0.2C rate = 26 mA, 0.5C rate = 65 mA, 1.0C rate = 130 mA, 2.0C rate = 260 mA) down to 2.8 V. The test at each rate was conducted on at least three LIPBs fabricated by the same process and thus the data reported below are averaged values.

3. Results and discussion

The formation results from three cycles at 0.05C are shown in Fig. 2. The higher charge capacity and lower reversible capacity on the first cycle indicate the formation of a solid electrolyte interface layer on the graphite surface by interaction with the electrolyte solution. Details of the reaction mechanisms have been reported by Yoshida et al. [9]. The charge curves display shoulders at 3.36 and 3.96 V which correspond to contribution of the Ni and Co components in $\text{LiNi}_{0.82}\text{Co}_{0.18}\text{O}_2$, respectively. The discharge curves also show two shoulders, at about 3.5 and 3.9 V, and the result from the same two components. According to the results



(a)



(b)

Fig. 3. First-cycle discharge capacities of LIPB at various C rates after formation step.

obtained from similar source of LiNiCoO_2 ($\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ [10] and $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ [11]), stability of the solid-state oxidation potential can be achieved by partial Ni-substitution of the Co component. That is high-efficiency utilization of LiNiCoO_2 may be accomplished with long-cycle life if cut off voltage in charging is set at 4.2 V.

Discharge capacity when using a DMC-containing electrolyte reaches 177, 175, and 173 mAh g^{-1} in first three cycles, respectively, whereas a LIPB with an EMC-containing electrolyte shows higher corresponding discharge capacities of 191, 188 and 186 mAh g^{-1} . It is here important to consider the practical discharge capacities in the voltage range 4.2–3.3 V that can supply the power required to operate portable electronics steadily. In this practical voltage range, the capacities for initial stages are about 168 mAh g^{-1} for DMC-containing and 180 mAh g^{-1} for EMC-containing electrolyte. The higher capacity with EMC-containing electrolyte is probably due to the embedding effect of EMC [9] that can convert to DMC as well as diethyl carbonate (DEC)

by the trans-esterification reaction, i.e. $2\text{EMC} \rightleftharpoons \text{DMC} + \text{DEC}$ during initial charging step. Using EMC-containing electrolyte solution, an equilibrium mixture of EMC, DMC, and DEC exists after the first charging, and may therefore display the additional effects of EMC and DEC, compared with that of sole DMC.

The EMC-containing electrolyte exhibits better C rate characteristics than the DMC-containing electrolyte as shown in Fig. 3. The first-cycle results of EMC-containing electrolyte shown that the rated discharge capacity reaches 98.5% at the 0.5C rate, 83% at the 1.0C rate and 70% at the 2.0C rate when the discharge capacity at the 0.2C rate is set at 100%. For a practical voltage cut-off of 3.3 V at which a steep decrease in capacity starts to occur, the rated discharge capacity with EMC-containing electrolyte reaches 90 (0.5C), 69 (1.0C), and 50% (2.0C), whereas that DMC-containing electrolyte is 74 (0.5C), 44 (1.0C), and 7% (2.0C). The trend of capacity decrease with increase in C rate when using EMC-containing electrolyte is in good agreement with the half-cell results when using the high-capacity cathode material $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($x < 0.2$) [12,13]. The capacity fading with cycling is more severe with DMC-containing electrolyte, as shown in Fig. 4. Thus, it is concluded that with respect to the effect of discharge rate on cycle performance, EMC-containing electrolyte is more advantageous than DMC-containing one.

4. Concluding remarks

The capacity and cycle performance is reported for a LIPB that is fabricated via a modified form of the Bellcore process. The LIPB uses commercially available $\text{LiNi}_{0.82}\text{Co}_{0.18}\text{O}_2$ as a high-capacity cathode material and an EC-based electrolyte solution containing either DMC or EMC. As expected, $\text{LiNi}_{0.82}\text{Co}_{0.18}\text{O}_2$ shows a practical discharge capacity of $\sim 180 \text{mAh g}^{-1}$ which is higher than that of conventional LiCoO_2 , and a better capability when using EMC-rather than DMC-containing electrolyte. The cycling behavior is also improved, particularly in high C rate tests. LIPBs fabricated and characterized by the present method could become commercial product through the development of more accurate cell-design and more precise processing techniques.

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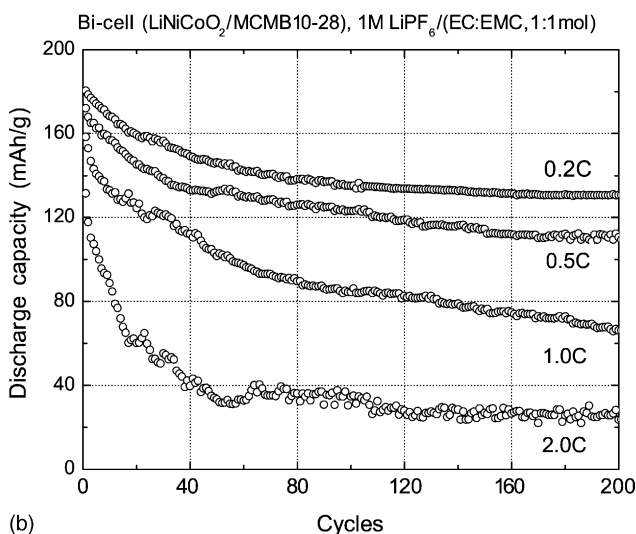
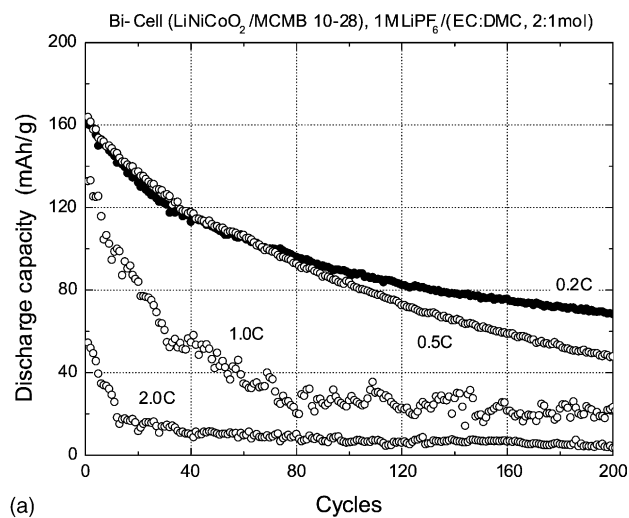


Fig. 4. Cycle performance of LIPB at various C rates.

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