Differential pulse effects of solid electrolyte interface formation for improving performance on high-power lithium ion battery

Fu-Ming Wang [a,b,*], Hsin-Yi Wang [b], Meng-Han Yu [c], Yi-Ju Hsiao [c], Ying Tsai [c]

[a] Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei, Taiwan
[b] Sustainable Energy Center, National Taiwan University of Science and Technology, Taipei, Taiwan
[c] Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan

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ABSTRACT

Solid electrolyte interface (SEI) formation is a key that utilizes to protect the structure of graphite anode and enhances the redox stability of lithium-ion batteries before entering the market. The effect of SEI formation applies a differential pulse (DP) and constant current (CC) charging on charge–discharge performance and cycling behavior into brand new commercial lithium ion batteries is investigated. The morphologies and electrochemical properties on the anode surface are also inspected by employing SEM and EDS. The electrochemical impedance spectra of the anode electrode in both charging protocols shows that the interfacial resistance on graphite anodes whose SEI layer formed by DP charging is smaller than that of CC charging. Moreover, the cycle life result shows that the DP charging SEI formation is more helpful in increasing the long-term stability and maintaining the capacity of batteries even under high power rate charge–discharge cycling. The DP charging method can provide a SEI layer with ameliorated properties to improve the performance of lithium ion batteries.

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1. Introduction

The demand of lithium ion batteries is increasing rapidly since they are playing an important role of power supplies for cellular phones, laptops, and other portable electronics. Graphite, the most popular anode in lithium ion battery, is usually employed which can prevent the dendrite of lithium compared to lithium metal causing short-circuit in the batteries and elicit high energy density during intercalation process [1]. During the first charge, lithium ions are extracted from the cathode and intercalated into the anode through a non-aqueous electrolyte such as ethylene carbonate (EC), propylene carbonate (PC), and ethyl methyl carbonate (EMC). The electrolyte containing lithium salt ($LiPF_6$) becomes easier to fabricate a complex layer including organic and inorganic compounds on the anode named solid electrolyte interface (SEI) or the passivation layer [2]. In fact, the properties of SEI film commend the performances of the batteries. The composition of SEI layer can be distinguished to several kinds of compounds including $LiCO_3$, $LiOH$, LiF, Li_2O, $ROCO_2Li$, and $ROLi$. Therefore, how to demonstrate the quantity and quality of SEI layer, either enhance cell performance or effectively improve safety, especially for future electric vehicle (EV) development. For example, solvent-based SEI layer was found which can exhibit a high thermo stability [3]. Xu pointed out the cyclic carbonate such as EC and PC depict an opposite interface deposition mechanism while SEI was growing on the graphite surface [4]. Zhang demonstrated that two electrons pathway for EC decomposing, and one electron pathway for PC since the electron donating group, –CH3, augments electron density within the cyclic structure [5], restricting the electron flowing to establish a useful organic compound like the pathway II shown in Fig. 1 [5,6]. A dynamic research using an electrochemical impedance spectroscopy (EIS) reveals that the SEI formation takes place at two major stages [7,8]. A porous, highly resistive and dimensionally unstable SEI layer grows at the first stage before the lithium ions intercalate into graphite, and the second stage takes place simultaneously with the intercalation of lithium ions, resulting in a more elaborated and conductive SEI layer. In addition, some additives containing carbon–carbon double bond in their molecules such as maleimide (MI) [9], vinylene carbonate (VC) [10] and vinyl ethylene carbonate (VEC) [11]. Those compounds with higher reduction potential are usually employed to fabricate organic SEI layers, preventing the donating chemicals such as PC from fracturing the structure of graphite.

The well functioned SEI is an electron insulator but provide excellent ionic conducting channels for lithium ions, diffusing

* Corresponding author at: IB 606, 43 Keelung Road, Section 4, Taipei 106, Taiwan.
Tel.: +886 2 27303755, fax: +886 2 27376922.
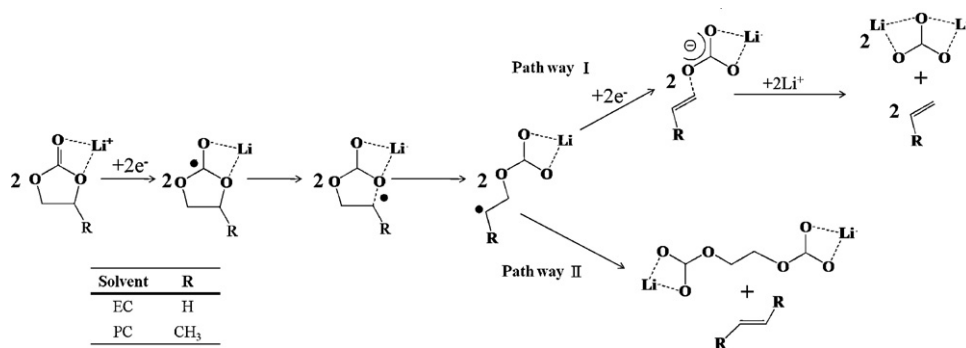E-mail address: mccabe@mail.ntust.edu.tw (F.-M. Wang).

Fig. 1. The decomposition mechanism of EC and PC [5,6].

into graphite anode. In general, the irreversible capacity at first charge–discharge cycle is utilized to form SEI layer, and the consumption of lithium ions and electrolyte is an irreversible reaction [12]. Although SEI layer causes a few of energy loss of the batteries at the first cycle; however, it enhances safety performance of batteries via suppressing the intercalation of solvent into graphite layers and protecting the structure from exfoliating. Normally, commercial batteries were charged and discharged of 1 cycle before entering to the markets and usually employs constant current (CC) charging to form SEI layer. The magnitude of current is an important factor since it dominates the chemical properties of the SEI. To form a fine and delicate construction of SEI layer which can altitudes the performance of the batteries, a low current rate charging is usually applied to prepare SEI layer. However, it will extend the charging time and consumption of electricity. Chiang et al. utilized a two steps different rate current charging for preparing SEI layer in order to eliminate the charging time [13]. Li et al. used pulse method to eradicate polarization of the batteries and enhance the power rate, thereby accelerated the charging process [14]. Therefore, the pulse and two steps changing may be useful and produce uniform SEI with better adherence to the graphite. In addition, Li et al. also discovered that the cycling ability of the batteries is better than that of CC charging.

In this paper, the charge–discharge characteristics, cycle performance, and electrochemical properties of lithium ion batteries with SEI film grown by differential pulse (DP) formation are performed and compared with that of traditional CC charging. The morphology and the compositions of SEI film prepared by both protocols are observed by SEM and EDS. Those data will guide a new concept to prepare an elaborate SEI layer in commercial lithium ion batteries.

2. Experimental

The lithium ion batteries used in this study were two electrode type 503709C cells provided from EXA Co. in Taiwan (ALB, aluminum–plastic laminated film exterior with dimensions of 5.0 mm × 37 mm × 59 mm) with capacity of 1360 mA h. The cathode consisted 91 wt% $LiCoO_2$ as active materials, 6 wt% PVDF as binder, and 3 wt% Ks-6 as conductive additive. The graphite anode composed 93 wt% mesocarbon microbeads (MCMB-2528, Osaka Gas), 4 wt% PVDF as binder, and 3 wt% Ks-6 as conductive additive. The electrolyte utilized here was 1.1 M lithium hexafluorophoshate ($LiPF_6$) in EC:PC:DEC (3:2:5 in volume ratio) and 2 wt% VC. The batteries were charged by the following programs: the batteries were CC charged at 0.1 C for 10 min, thus subjected to DP with a pulse magnitude of 0.2, 0.5, or 1 C with 1.5 ms duration and charging of 0.5 ms to 4.2 V, and constant voltage charged maintain at 4.2 V until the current is below to 0.01 C. Those batteries were then discharged by 0.2 C to 2.75 V. According to the literature, typical characteristic of DP charging are shown in Fig. 2. Three parameters include the
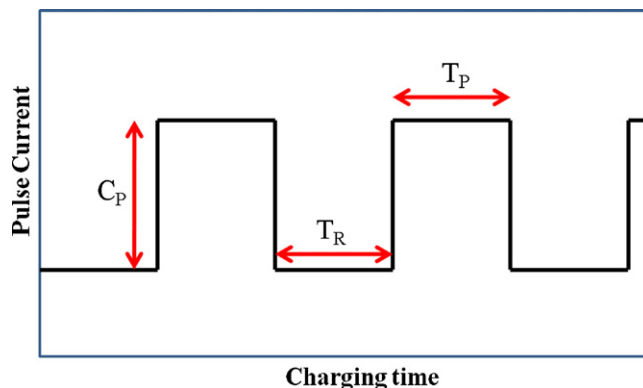

Fig. 2. A typical current variation curve of pulse charging including resting duration between pulses (T_R), the magnitude of pulse current (C_P), and the pulsing time (T_P).

duration time (T_R), the magnitude of the pulse (C_P), and the charging time (T_P). A long duration, low pulse magnitude, and long charging time prolong the charging process since it will take a lot of time to accumulate the capacity. In our case, a new DP method has been developed for the SEI formation, in order to avoid the polarization takes place during SEI fabrication and shorten the charging period. Appropriate 1.5 ms duration and charging of 0.5 ms are therefore already designed as T_R and T_P, respectively.

On the other hand, the controlled group of batteries were charged on the following program: the batteries were CC charged at 0.1 C for 10 min, then subjected to CC charging at 0.2, 0.5, or 1 C to 4.2 V, and constant voltage charged maintain at 4.2 V until the current below to 0.01 C The batteries were then discharged at 0.2 C constant current rate to 2.75 V. The charging program and the code name of batteries are listed in Table 1.

The morphologies and compositions of the MCMB electrodes dissembled from 503709C cells were observed by scanning electrodes microscopy (SEM, JSM-6480 JEOL), and energy dispersive

Table 1
The charging program of DP and CC charging for SEI formation.

| Cells (number)	Charging protocol
P1	0.1 C CC charging for 10 min → 0.2 C pulse charging to 4.2 V → CV charging to 4.2 V
P2	0.1 C CC charging for 10 min → 0.5 C pulse charging to 4.2 V → CV charging to 4.2 V
P3	0.1 C CC charging for 10 min → 1 C pulse charging to 4.2 V → CV charging to 4.2 V
C1	0.1 C CC charging for 10 min → 0.2 C CC charging to 4.2 V → CV charging to 4.2 V
C2	0.1 C CC charging for 10 min → 0.5 C CC charging to 4.2 V → CV charging to 4.2 V
C2	0.1 C CC charging for 10 min → 1 C CC charging to 4.2 V → CV charging to 4.2 V
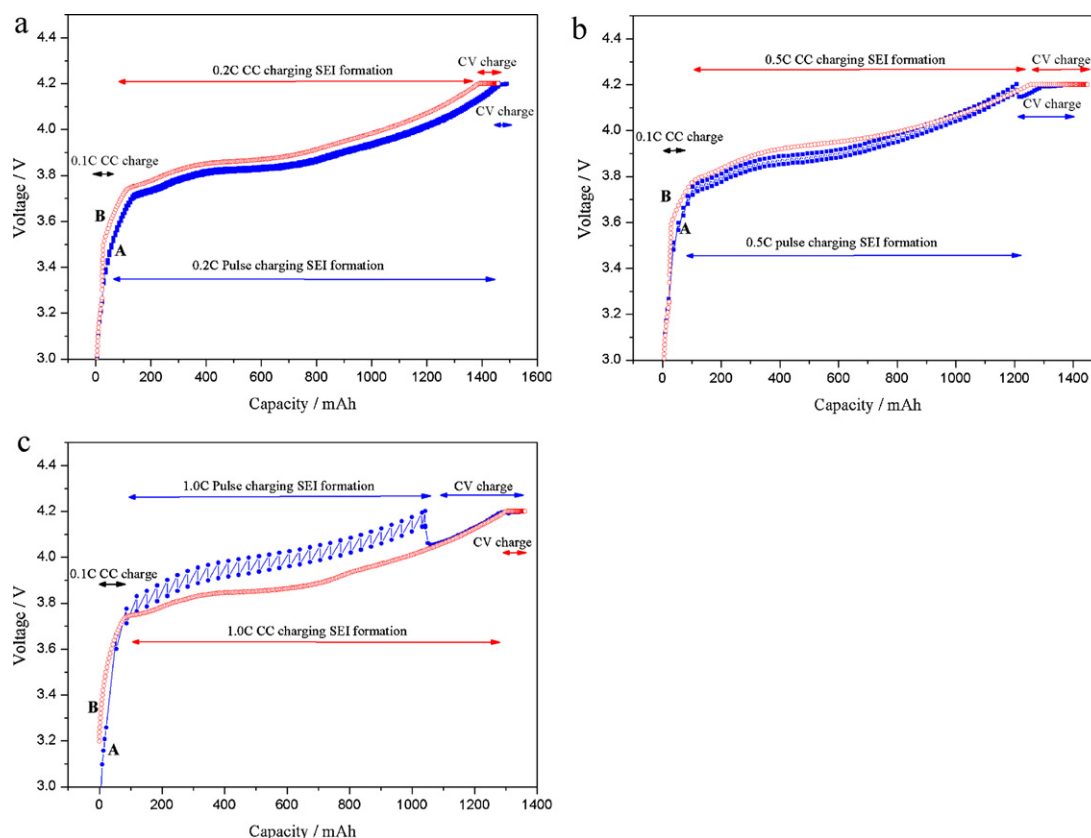
Fig. 3. Charging curves during SEI formation of cell: (a) P1 in (A), C1 in (B), (b) P2 in (A), C2 in (B), and (c) P3 in (A), C3 in (B).

spectrometer (EDS) on a LEO-1530 at an accelerating voltage of 10 and 15 keV. The MCMB electrodes were washed by DMC in the dry room and dried in a vacuum for 24 h before observations. The electrochemical impedance spectroscopy (EIS) was employed a Solatorn impedance analyzer (SI-1260) in combination with an electrochemical interface (SI-1286) potentiostat/gavanostat in the frequency range from 100 M to 0.01 Hz with AC amplitude of 5 mV at 25 °C. To inspect the cycling ability, those batteries with two different protocols, differential pulse and constant current, were further CC charged at 0.2 C and discharged at 0.2, 0.5 and 1.0 C for 50 cycles by a Maccor Battery Tester series 4000.

3. Result and discussion

3.1. Charging characteristics with two methods of SEI formation

Fig. 3 shows the charge curves of SEI formation of batteries with DP and CC methods at 0.2, 0.5 and 1 C. At the 0.2 C, Fig. 3(a) states the average working voltage of DP charging (3.81 V) is slightly lower than CC charging (3.88 V). However, the charging capacity via DP charging can be extend compared to CC charged. In addition, the entire charge curve with pulse method reveals a lower voltage ten-

dency behavior, indicating that lower current pulse charged the cathode more efficiently by erase the activation and concentration polarizations. Fig. 3(b) shows similar charge curve with 0.5 C pulse charging compared to the CC charging. Compares in 1 C results, Fig. 3(c) illustrates the charge curve with pulse method quickly thrusts to the ending voltage (4.2 V) and changes to constant voltage charging model caused by the polarization increased.

The charge–discharge performances of batteries with those of SEI formations are summarized in Table 2. It reveals that the battery capacity reversible ratios of DP charging at different rates are all higher than that of CC charging. However, only the 1 C DP and CC charging protocols show their discharging capacities are less than 1300 mA h, indicating that the 1 C charging is not suitable and leads about serious activation and concentration polarization effects [15]. According to this reason, the over loading pulse current (C_P) cause an ominous vibration of voltage likes Fig. 3(c), which may influences the structure of SEI and the intercalation stability to the anode material. Therefore, 0.2 C (1441.3 mA h) or 0.5 C (1360.4 mA h) DP charging reveals better discharging performance and shows an applicable SEI formation. In addition, the batteries prepared by high current charging condition (cells P3 and C3) are thereby excluded in the following electrochemical measurements.

Table 2
The charge and discharge capacities of first cycle of batteries.

Cells (number)	First charge capacity (mA h)	First discharge capacity (mA h)	Reversible capacity (%)
P1	1489.7	1441.3	96.8
P2	1417.4	1360.4	95.9
P3	1342.7	1285.3	95.7
C1	1458.6	1384.2	94.9
C2	1448.9	1374.6	94.9
C2	1363.3	1292.5	94.8
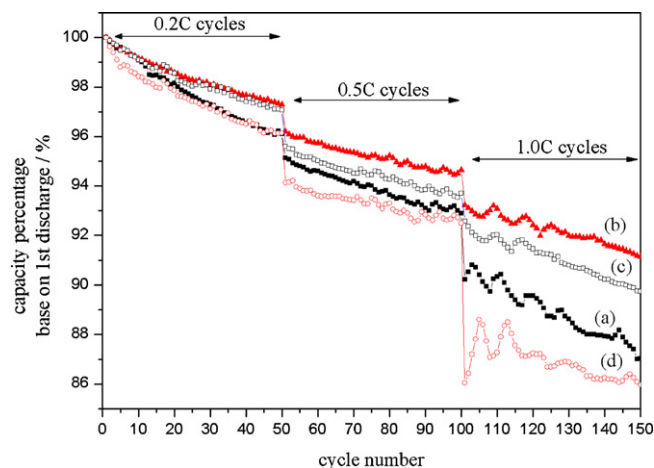
Fig. 4. Cycle characteristics at various charging rates of the cells: (a) P1, (b) P2, (c) C1 and (d) C2.

Fig. 5. Impedance results (solid spot) and simulating results (hollow spot) of the cells: (a) P1, (b) P2, (c) C1 and (d) C2.

3.2. Cycle life characteristics

Fig. 4 displays a cycle life measurement of the batteries by using DP and CC SEI formations. Interestingly, cell P2 with DP formation shows an extremely higher and stable cycle ability and lower fade capacity performance than others at three different discharge currents. However, cell P1 does not exhibit better capacity and becomes worse at high power discharge test (1 C), suggesting that the 0.5 C DP provides a unique behavior which is the behavior of periodically pausing rest for lithium ionic transfer to fabricate an organic SEI. On the contrary, 0.2 C DP cannot provide suitable protection for the battery due to the magnitude of pulse is not strong enough. Nevertheless, the cell C1 with slow CC charging shows well delicate SEI structure thereby exhibits good cycling performance due to a lower continuing current which would not polarize the electrochemical reaction to the anode and the electrolyte with additives, causing a tremendous concentration polarization of the battery. Therefore, a fast CC charging is not appreciated for SEI formation in lithium ion battery like the cell C2. Besides, cell P2 not only shows higher cycle stability than others at different rate cycles, but also remains its capacity retention more than 91% after 150 cycles, demonstrating that the SEI formation of 0.5 C DP can effectively protect MCMB electrode and hold reliable electrochemical properties during high power cycling test.

3.3. EIS analysis

In order to realize why the cycling ability of the batteries reveals a huge difference with various SEI layers prepared by DP and CC charging protocols, the impedance analysis is applied to identify the effects of the SEI formations. Fig. 5 shows the EIS results measured after cell formatted by two protocols and discharged to 2.75 V. An equivalent circuit model shown in Fig. 6 represents the internal construction of the battery which is divided into five items, including series resistance (R_S) represented the wire and electrolyte resistances, the first resistance–capacitance (RC) element represented the impedance of SEI layer, the second RC circuit caused by the interface between the SEI layer and the anode surface, Warburg element (Z_W) reflecting the ionic diffusion resistance of bulk cathode, and the interface capacitance (C_0) [16]. The simulation result is summarized in Table 3. Because all batteries employed same electrolyte and electrode materials, the R_s are thereby approximately the same.

However, all DP charging of SEI formations show lower R_1 value compared to CC charging, indicating the SEI possesses uniform
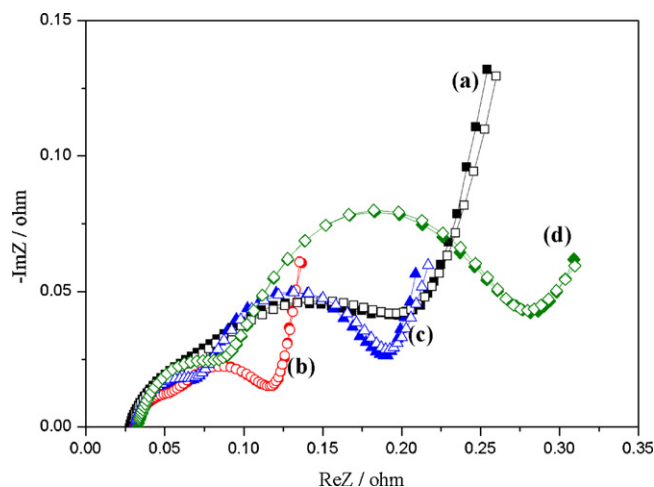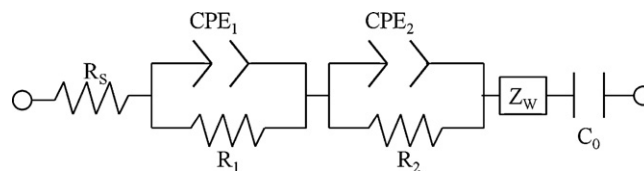

Fig. 6. The equivalent circuit model used to interpret the internal battery construction.

spherical microstructures which provides low resistance, excellent ionic diffusivity and thin thickness. In addition, the R_1 of P2 cell (19.1 mΩ) indicates a lower value than P1 (27.3 mΩ) which is opposite to C1 (42.8 mΩ) and C2 (60.2 mΩ) cells, respectively. This evidence proves that 0.5 C DP charging formation illustrates a unique SEI fabrication with a short pausing process for a useful thin layer of SEI than 0.2 C CC charging. R_2 value represents the lithium-intercalation resistance of the interface between the SEI and MCMB electrode. A well-functioned SEI layer can provide a suitable channel for lithium ion intercalating. The R_2 of P2 cell shows lower contact resistance (65.5 mΩ) than others while SEI was formed on the electrode surface, indicating that correct infrastructures can be predicted like high uniformity and high diffusivity of SEI and interface without critical transition layer. P2 cell possesses lowest R_2 value also indicates those SEI layers prepared by 0.5 C DP charging exhibit as the good ionic conductors. Nevertheless, a high R_2 value of P1 cell reveals that the SEI prepared by 0.2 C DP charging still not able to provide suitable channel for lithium ionic diffusing. The bulk electrode diffusivity of Z_w indicates that P2 cell provide excellent ionic intercalation and de-intercalation with the lowest value. According to above EIS analysis, the P2 cell furnishes the best cycling performance is determined by a series of reasons which are the resistance, composition, uniformity, thickness and ionic diffusivity of SEI.

Table 3
Values of the parameters in the equivalent circuit from the simulation result.

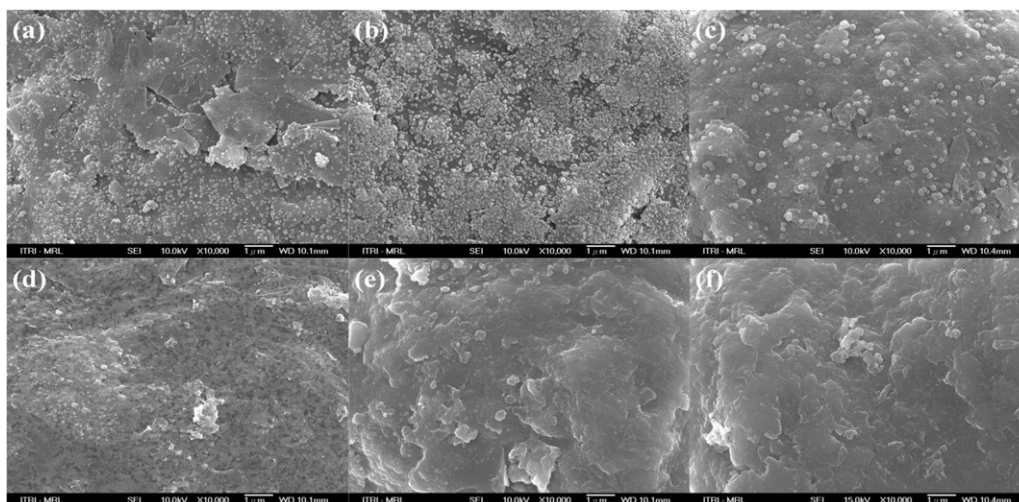| Cells (number)	R_S/mΩ	R_1/mΩ	R_2/mΩ	Z_W/mΩ S$^{-0.5}$	C_0/F
P1	28.4	27.3	143.9	15.9	186.1
P2	32.1	19.1	65.5	4.9	396.7
C1	30.6	42.8	107.2	8.9	736.6
C2	32.6	60.2	163.7	13.6	20,244

Fig. 7. SEM images of the MCMB electrode surfaces of cell: (a) P1, (b) P2, (c) P3, (d) C1, (e) C2 and (f) C3.

Table 4
The EDS results of SEI layers prepared by DP and CC charging formation.

Cells (number)	Carbon atomic percentage (%)	Oxygen atomic percentage (%)	Fluorine atomic percentage (%)
P1	89.9	4.2	5.8
P2	92.4	2.4	5.2
P3	94.3	2.7	2.9
C1	81.8	13.4	4.8
C2	82.6	12.4	5.1
C3	91.1	6.2	2.7

3.4. Morphological and structural analysis of MCMB electrodes

The MCMB electrodes with different types of SEI formed by two charging protocols were disassembled from the batteries. The microstructures and the compositions of individual electrodes were inspected by SEM and EDS. Fig. 7 shows that the SEI on the MCMB surface with 0.2 C DP charging reveals some of Ks-6 flakes dispersed which represents the SEI does not totally cover onto MCMB surface. By increasing the magnitude of pulse, the SEI outs more covers and fullness over the MCMB which are shown in Fig. 7(b) (0.5 C) and (c) (1 C). In addition, Fig. 7(c) also indicates some of little white spots of SEI fabricated, but the number of the spots is less than that of 0.5 C. The reason causing the little white spots of SEI microstructures for the DP charging formation is still unclear, but we believe that the electrolyte concentration gradient takes place during the formation and a short period equilibrium of the concentration distribution causes SEI into a three dimensional nano channel. As the SEI formation of CC charging, all morphologies show flat and smooth MCMB surface, but much thicker by increasing the current. The compositions of SEI layers examined by EDS are listed in Table 4. Carbon, oxygen and fluorine are the three main components of atoms usually existing in the SEI layer.

According to this table, the SEI formed by DP charging exhibits extremely lower oxygen content compared to that of SEI layers formed by CC charging. In addition, the carbon concentration of SEI formed by DP formation reveals higher content in the structure. For example, the P2 cell has 92.4% of carbon than 82.6% of C2 cell. Furthermore, fluoride element shows approximately the same value in two of different charging protocols, indicating the formation technique indeed affects the composition of SEI.

Previous literatures illustrate that the solvent-based SEI exhibits higher thermo and kinetic stability than salt-based SEI. Generally, the solvent-based organic components including alkyl groups or polycarbonate enlarge the percentage of carbon and reduce the percentage of oxygen in the SEI layer. On the contrary, the salt-based of inorganic compounds like Li_2O, Li_2CO_3 and LiOH contain more oxygen atoms than carbon atoms, which are increasing the oxygen ratio of SEI layers. Therefore, the DP charging formation at 0.5 C provides more useful and organic compounds for enhancing the diffusivity of ionic transfer.

By above results, the composition of SEI layer is not only strongly influenced by the temperature [14], aging condition [17] and charging voltage [7,8], but also affected by the charge types of battery formation.

In addition, this study used a typical carbonate electrolyte and a two electrode commercial type battery for differential pulse (DP) formation of SEI and battery performance measurements. In order to precise interpretation regarding SEI formation in the first charging range of battery and fit in with EIS speculation; a new three electrode cell system with Li reference electrode and other carbonaceous materials are being designed for further research.

4. Conclusion

This research regarding a differential pulse (DP) formation of SEI and the two electrode commercial type battery performance analysis has been developed. The battery applied with 0.5 C DP formation shows excellent battery performance not only the cycle ability but also the power characters also be dramatically enhanced. Compared to normal constant current (CC) of SEI formation, this technique provides enough competitiveness for application to the coming electric vehicle (EV) market. Moreover, this result suggests that the charging type also affect the composition and ingredient of SEI layer in different dynamic way.

Acknowledgements

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