



Short communication

Decreasing the initial irreversible capacity loss of graphite negative electrode by alkali-addition

Atsushi Sano*, Masato Kurihara, Kazuya Ogawa, Tsuyoshi Iijima, Satoshi Maruyama

TDK Corporation, Device Development Center, 570-2 Matsugashita, Minamihatori, Narita-shi, Chiba, 286-8588, Japan

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ABSTRACT

The effect of alkali function group contained in electrode binder was investigated. Carboxy methyl cellulose (CMC) improved the initial irreversible capacity loss in graphite negative electrode. Lithium acetate also improved the initial cycle efficiency. On the other hand, ethyl cellulose (EC) and hydroxyl propyl methyl cellulose (HPMC), which do not have a carboxylic group, did not decrease the reductive electrolyte decomposition. After charge and discharge cycle, the surface film composition on the electrode with CMC was less than on the electrode without CMC. This suggests that a carboxylic group in the binder acted as a catalyst and promoted the solid electrolyte interphase (SEI) formation which prevents the excess electrolyte decomposition on the graphite electrode.

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1. Introduction

Recent research on lithium-ion batteries has been motivated mainly by electric vehicles and hybrid electric vehicles that decrease the environmental burden. To meet the power demand of such electric vehicles, large-size lithium-ion batteries are being studied. Small-size lithium-ion batteries already have been commercialized and have led to the expansion of the production of portable electronic devices. These portable devices have made great progress in acceptance and their increased size has resulted in an increase of power consumption, and they therefore require higher energy densities for the small-sized lithium-ion batteries. Almost all commercial lithium-ion batteries employ graphite negative electrode which has a potential as low as lithium metal. Graphite negative electrodes possess other advantages such as low cost, good cycle ability, low volume expansion, safety, etc.

One of the disadvantages of the graphite negative electrode is the irreversible capacity at the first cycle. When lithium-ion intercalates into graphite electrode, the potential is almost identical with that of lithium metal as mentioned above, and therefore, most organic compounds decompose at this low potential. It is very well known that the decomposition of electrolyte at graphite electrode leads to the formation of a passivation film described as solid electrolyte interphase (SEI) [1]. The irreversible capacity is principally

due to the decomposition of the electrolyte to form SEI. Once SEI is fabricated at the graphite electrode, further decomposition of the electrolyte is greatly suppressed, resulting in almost 100% coulombic efficiency. SEI is essential for the stable charge and discharge reactions of lithium-ion batteries. However, the irreversible capacities cause a decrease in the energy densities of lithium-ion batteries, and therefore, the irreversible capacities must be minimized.

To reduce the irreversible capacity the SEI has been extensively studied by many researchers in the method of FT-IR [2–4], XPS [5,6], GC/MS [7,8], NMR [9], XAFS [10], etc. These reports suggested that the SEIs are mainly comprised of ROCO_2Li or Li_2CO_3 or a PEO-like polymer or the complexes of these inorganic and organic compounds. Aurbach et al. [11] improved the cycle performance of graphite negative electrode using CO_2 as an additive. They concluded that CO_2 promoted the precipitation of Li_2CO_3 , which is one of the most efficient passivating agents, on the graphite negative electrode. SEI growth at elevated temperatures was observed by AFM. Inaba et al. [12] reported that SEI grew significantly during the charged state. This caused irreversible capacity at the following cycles.

Many additives for electrolytes and for electrodes have been investigated in looking for effective ways to reduce the irreversible capacity at the initial charging state. Among them, vinylene carbonate is one of the additives, which has been commercialized in lithium-ion battery markets. Other additives of sulfuric compounds such as ethylene sulfite (ES) and 1,3-propane sultone (PS) have been studied. These additives are reduced at higher potential prior to electrolyte decomposition, and then additive-derived SEIs are formed, resulting in a decrease in irreversible capacities.

* Corresponding author. Tel.: +81 476 37 1611x7628; fax: +81 476 37 1688.

E-mail address: sanoa@jp.tdk.com (A. Sano).

Another approach to suppress the irreversible capacities is coating of the graphite negative electrode. Coatings of inorganic compounds such as Li_2CO_3 , Na_2CO_3 , and NaClO_4 and also the metals Sn and Si have been reported to be very effective in decreasing the irreversible capacities and improving the cycle performance [13–15].

A recent study by Buqa [16] has revealed that a binder affects the irreversible capacity. Carboxymethyl cellulose (CMC) sodium salt as a binder improved irreversible capacity loss compared with poly(vinylidene fluoride) (PVdF). This result is remarkable in that the binder decreases the first capacity loss. The mechanism leading to this decrease is not clear.

We investigated the effect of binders and additives for the electrode by means of cyclic voltammetry, charge and discharge, AES and TOF-SIMS. We focused on the effect of alkali and the mechanism of SEI formation.

2. Experimental

Synthetic graphite powder (Hitachi chemical) was used for cyclic voltammetry and charge/discharge tests. The graphite powder (92 wt%) was mixed with a 7 wt% poly(vinylidene fluoride) (PVdF) (Kureha chemical) and CMC (1 wt%) using 1-methyl-2-pyrrolidinone as a solvent. The mixed slurry was coated on Cu foil (thickness: 16 μm) by doctor blade method. The coated film was dried at 110 °C and roll pressed. Ethyl cellulose (1 wt%), instead of CMC, was used in the same process.

Hydroxy propyl methyl cellulose (HPMC) was used to improve viscosity. Synthetic graphite (95.2 wt%) and 2.5 wt% styrene butadiene rubber (SBR) (JSR) and 1.5 wt% HPMC (Shinetsu) were dissolved in distilled water. Lithium acetate (0.8 wt%) was added to the slurry. This slurry was coated on Cu foil, dried and pressed.

For the positive electrode, $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (Seimi Chemical) (94 wt%) was mixed with a 3 wt% PVdF Kureha chemical and 3 wt% acetylene black (Denki Kagaku Kogyo) with NMP. The mixed slurry was coated on Al foil (thickness: 15 μm), dried and pressed.

For the evaluation, a 3 electrode Al laminated cell was used. The working graphite electrode was cut 12 mm on a side. Lithium metal (Honjo metal) was used as the counter electrode and reference electrode. 1 mol dm^{-3} $\text{LiPF}_6/\text{PC} + \text{EC} + \text{DEC}$ (2:1:7) (UBE) added to 2 wt% 1,3,2-dioxathiolane-2,2-dioxide (DTD) (Aldrich) was used as the electrolyte. The electrolyte contained less than 20 ppm water as measured by Karl–Fisher-titration.

For cyclic voltammetry, Potentiostat HA-301 and function generator HB-104 (Hokuto denko) were used. The sweep rate was 5 mV s^{-1} . Cut off potential was 3.0–0 V.

Charge and discharge unit HJ101SM6 was used. Current density was 130 $\mu\text{A cm}^{-2}$.

The morphology of the electrode was observed by scanning electron microscopy (SEM), and the mapping of elements was measured by Auger electron spectroscopy (AES) and time of flight secondary ion mass spectrometry (TOF-SIMS).

3. Results and discussion

A cyclic voltammograms (CVs) are shown in Fig. 1. The cathodic current peak was observed at 0.8 V in CMC 1 wt% for both the CMC-contained and CMC-free electrode. This cathodic current peak should be the decomposition of PC [18]. The peak at about 0.55 V appeared at the CMC 1 wt% electrode. This peak vanishes in the case of CMC-free electrode. It may be related to the reduction of CMC and electrolyte. Compared the CVs with the mentioned above, the anodic current is different. The anodic current of CMC 1 wt% is larger and the potential of the peak is lower than for the without CMC. This indicates that low resistance SEI was formed because of low polarization due to the addition of CMC 1 wt%.

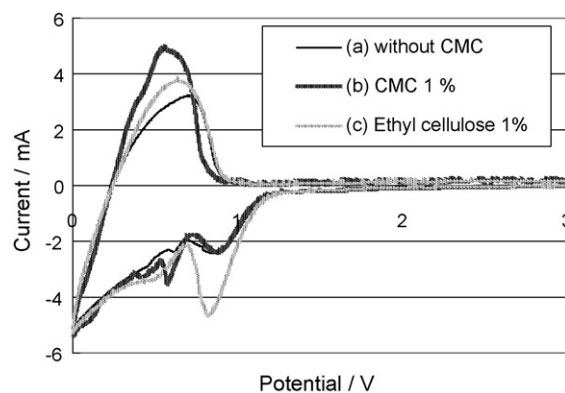


Fig. 1. CV of graphite electrode mixed with (a) CMC 0%, (b) CMC 1% and (c) ethyl cellulose 1% (1st cycle, scan rate 5 mV s^{-1}).

Instead of CMC, ethyl cellulose was also added into the electrode. The CVs of ethyl cellulose 1 wt% showed a large cathodic current at 0.8 V. This cathodic current peak is thought to be the decomposition of PC [18]. Ethyl cellulose increased the PC decomposition whereas CMC decreased the PC decomposition. CMC has a carboxyl group and ethyl cellulose does not. This indicates that the difference caused by the functional group binder is the carboxyl group. Our investigation of the effect of the carboxylic group will be discussed later.

Charge and discharge curves are shown in Fig. 2. In the initial charging stage at 2.3–2.0 V, the plateau of the without CMC is larger than for the CMC 1 wt%. This plateau is thought to be the decomposition of DTD [17]. Some sulfuric compounds have decomposition potentials of around 2 V [18]. The charging capacity of CMC 1 wt% below 1.0 V was smaller than that of without CMC. The irreversible capacity below 1.0 V is due to electrolyte decomposition and precipitation [19]. This result suggests that the addition of CMC decreased the decomposition of the electrolyte. The initial efficiency is improved from 88% to 92% by CMC addition.

On the other hand, ethyl cellulose depressed the initial efficiency to 73% of the original. There is a large plateau below 0.8 V and discharge capacity is lower than for the without CMC and CMC 1 wt%. The existence of ethyl cellulose might prevent smooth SEI formation.

Fig. 3 shows CMC concentration dependence on initial cycle efficiency. For CMC 1 wt%, the initial efficiency was maximum. We

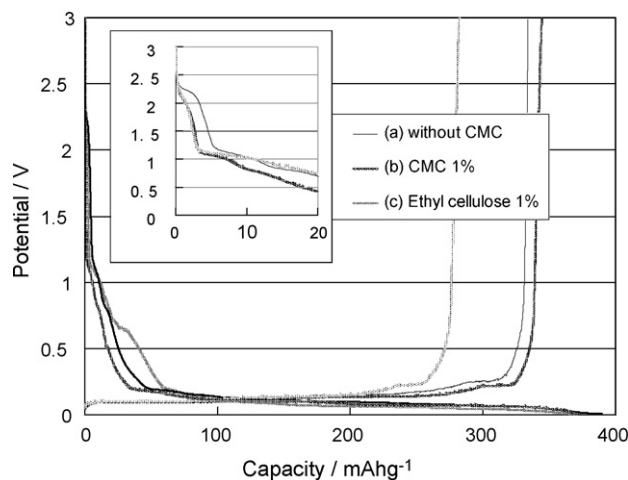


Fig. 2. Charge and discharge curves of graphite electrode mixed with (a) CMC 0%, (b) CMC 1% and (c) ethyl cellulose 1%.

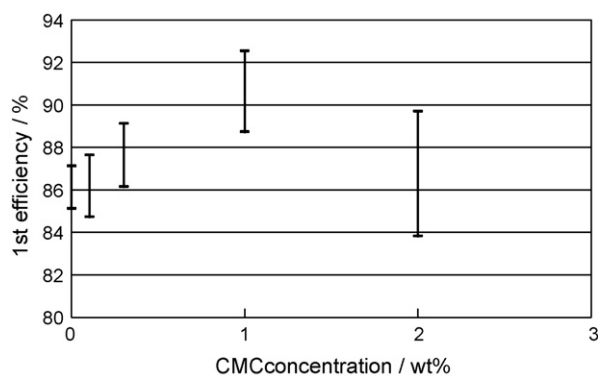


Fig. 3. Relationship of CMC concentration and 1st cycle efficiency.

think that the lower concentration was not sufficient to form SEI effectively. At higher concentration, the adhesive strength between active material and current collector was decreased. This might cause the low efficiency.

Fig. 4 is the cycle performance of without CMC and CMC 1 wt%. In this experiment, $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ was used as the counter electrode. At initial cycle, an increase in capacity was observed in without CMC. After 15 cycles, the capacity degradation in CMC 1 wt% was less than that in without CMC. This difference in cycle performance indicates that the difference in SEI formation in the initial cycle affects the cycle performance thereafter.

Two reasons were considered for the improvement of the initial cycle efficiency by CMC addition. Sodium ions contained in the CMC could behave as an additive for the electrolyte [20]. Another reason is that the anion in the CMC affects the SEI formation. To separate the reasons, we used a no carboxyl group containing binder HPMC, and we added lithium acetate to the electrode.

Fig. 5 shows the charge and discharge curves. The broken line shows the no alkali containing binder. The solid line shows the 0.8 wt% lithium acetate. In first cycle charging stage, no alkali electrode had a larger plateau below 1.2 V than the 0.8 wt% lithium acetate electrode. Discharge capacity of the no alkali electrode was lower than that of the lithium acetate electrode. This result shows that lithium acetate prevents solvent decomposition and reduces the first irreversible capacity. It is thought that lithium-ion in lithium acetate did not affect the SEI formation. Thus acetate anions would have affected the first cycle efficiency.

The CVs of lithium acetate is shown in Fig. 6. In this experiment, the electrode did not contain active material. Only a polymer or a

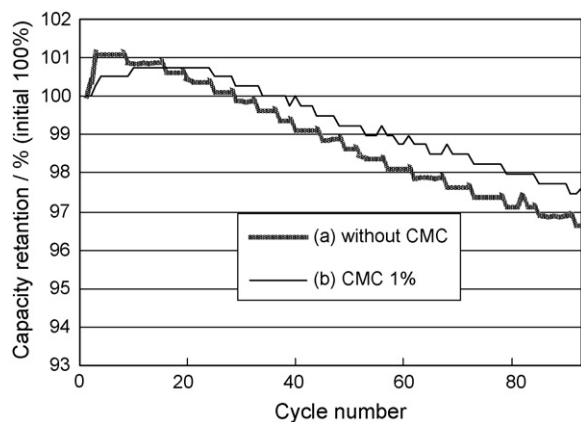


Fig. 4. Cycle performance of graphite electrode (a) without CMC and (b) CMC 1% (positive electrode $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$).

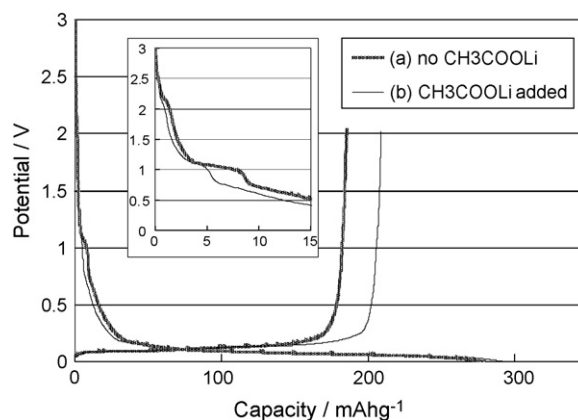


Fig. 5. Charge and discharge curves of graphite with (hydroxypropyl) methyl cellulose (a) no CH_3COOLi , (b) CH_3COOLi added in 1 M $\text{LiPF}_6/\text{PC}+\text{EC}+\text{DEC}$ (1:1:1)+5 wt% DTD.

salt contained polymer was coated on the copper foil. The broken line is HPMC, and the solid line is 1 wt% lithium acetate containing HPMC. The shapes of the curves are almost the same below 2.0 V. The broken line has a slight peak at 2.2 V, while there is no peak in the solid line. The difference between the two curves is shown in bold line as the ratio of the two curves. From this ratio, the difference between the two curves is the peak at 2.2 V. This suggests that lithium acetate affects the initial reduce reaction of the electrolyte additive DTD.

Fig. 7 is SEM images of a CMC mixed electrode. There is an agglomeration of CMC in the electrode. The size of the agglomeration was more than 100 μm . On the small scale view, the CMC does not seem to have coated the graphite. Sodium was not detected in points and mapping images using AES.

The agglomeration (20–30 μm) of Na was observed with TOF-SIMS (Fig. 8.) This result matches the SEM images. CF , C_3HF_4 and $\text{C}_3\text{H}_2\text{F}_6$ were detected. These fragmentations originated from PVdF binder. Comparing the fragment distributions of CMC and PVdF, the distributions were quite different. The PVdF distribution was uniform and the CMC was like a dot. The difference is because the CMC does not dissolve in NMP. Though CMC does, it is not uniform, CMC does affect the formation of SEI. Further analysis is needed to confirm the mechanism.

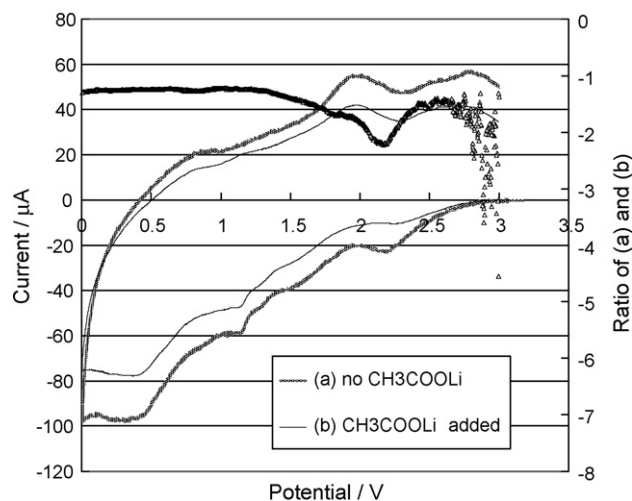


Fig. 6. CV of hydroxypropylmethylcellulose (a) without CH_3COOLi and (b) with CH_3COOLi (coated on Cu foil) (1st cycle, 5 mV s^{-1}).

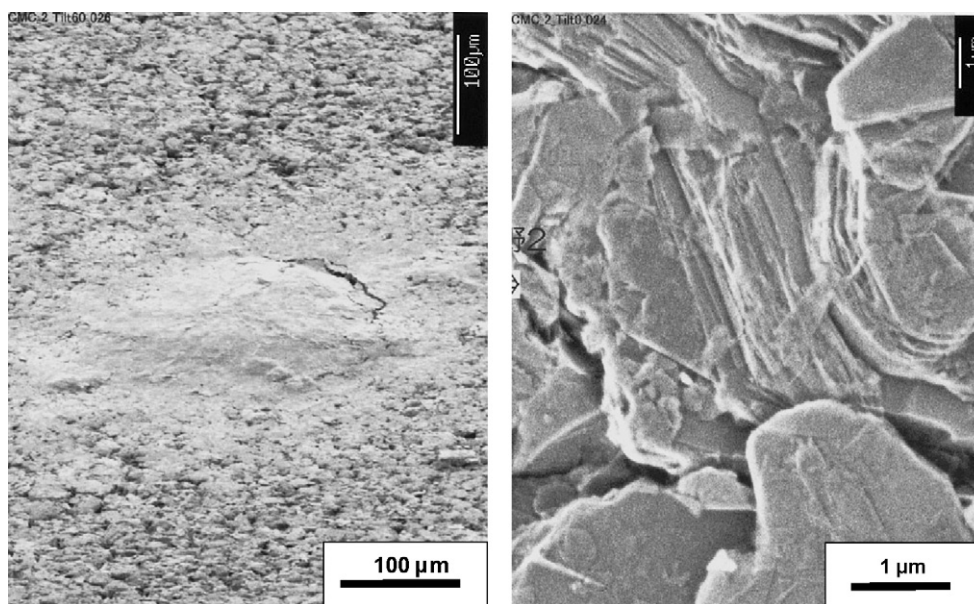


Fig. 7. SEM images of CMC containing electrode.

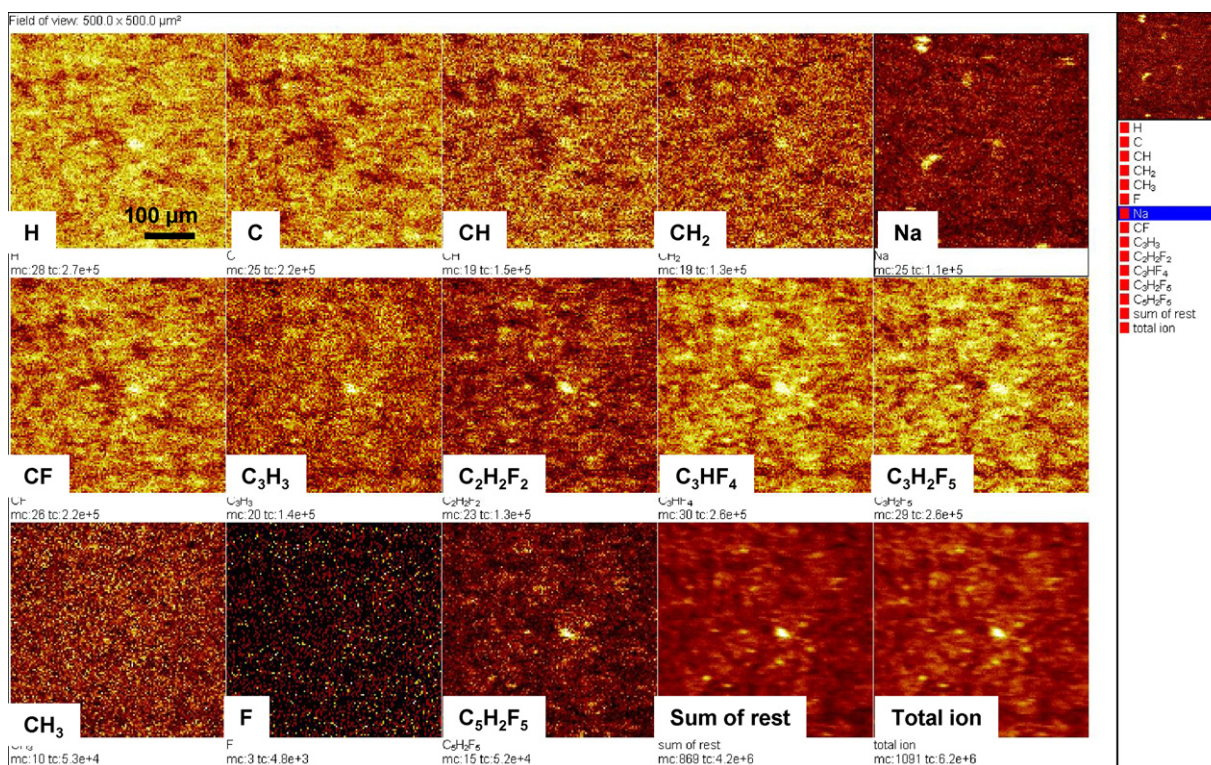


Fig. 8. TOF-SIMS mapping images of CMC containing electrode.

Table 1

TOF-SIMS intensity of fragmentation of the electrode charged and discharged in 1 M LiPF₆/PC + EC + DEC (1:1:1) + 5 wt% DTD.

Posi	Li	Na	Li ₃ O	NaLiF	Li ₃ F ₂	Li ₅ F ₄	Li ₃ SO ₄		
No addition	100	19.6	4.3	4.2	16.4	1.7	5.8		
CMC added	100	28.7	2.7	7.2	21.2	2.4	2.7		
Nega	F	S	HS	SO ₂	Li ₂ F ₃	SO ₃	SO ₄ H	LiSO ₄	C ₅ H ₃ SO ₂
No addition	100	1.6	1.0	11.7	5.9	24.6	11.3	12.7	5.1
CMC added	100	0.9	0.4	5.1	7.5	13.7	5.8	6.9	6.3

Table 1 shows the intensity ratio of TOF-SIMS fragmentation, normalized by Li^+ cation and F^- anion. The electrode for this analysis was charged and discharged. By positive fragment, Li_3O , NaLiF , Li_3F_2 and Li_5F_4 is larger in the CMC added electrode than in the no addition electrode. By negative fragment, SO_2 , SO_3 , SO_4H and LiSO_4 are larger in the no addition electrode than in the CMC added electrode. These results show that the CMC addition electrode increases the Li containing inorganic surface film and CMC addition decreases the sulfur containing surface film. These results correlate with the result of Fig. 6. In Fig. 6, CMC addition decreased the peak current at 2.2 V corresponding to DTD reduction. This indicates that CMC addition promoted the smooth formation of SEI and less sulfur compounds.

However the sulfur intensity of the CMC added electrode was about half that of the no addition electrode. $\text{C}_5\text{H}_3\text{SO}_2$ was larger in the CMC added electrode than in the no addition electrode. $\text{C}_5\text{H}_3\text{SO}_2$ is the reaction product of DTD. We think that CMC promoted the reaction of DTD to form more molecular weight compounds which act as effective SEI.

One possible reaction mechanism is that CMC promoted smooth SEI formation and prevented the excess decomposition of electrolyte. From the CVs of lithium acetate, the carboxylic group decreased the excess reaction of DTD.

Soos et al. reported ring opening oligomerization of PC and EC. PC forms a poly propylene oxide unit by ring opening reaction [21]. And EC forms a poly ethylene oxide unit. They reported that KHCO_3 or other alkali compounds were effective as the catalyst for polymerization. Ogumi et al. indicated that SEI on the negative graphite electrode contains PEO like compounds [8].

These results suggest that CMC or other alkali compounds acted as the catalyst to form polymer SEI and prevented the extra electrolyte decomposition.

SEM image and AES revealed that CMC exists inhomogeneously. The question remains as to whether inhomogeneous compounds affect the distant active materials or not. We could not detect CMC from electrolyte, but it may be possible that some part of CMC dissolved in the electrolyte and was absorbed in the electrode. Further investigation is needed in this area.

4. Conclusions

We investigated the effect of alkali compounds in a graphite negative electrode. CMC combined with PVdF improved the first

irreversible capacity loss in an electrolyte containing DTD. It also improved the cycle performance. To investigate the reaction of alkali compounds, we chose lithium acetate and hydroxyl propyl cellulose as binder. A lithium acetate containing binder decreased the reduction current peak at 2.2 V which is thought to be DTD reduction current.

By SEM, AES and TOF-SIMS measurement, it was revealed that CMC existed inhomogeneously. But CMC significantly affected the first cycle reduction of electrolyte. In the electrode with CMC after charge and discharge cycle, the composition of SEI measured by TOF-SIMS contained less sulfuric compounds and more DTD dimer like compounds than the electrode without CMC.

These results suggest that alkali compounds promote the reduction of DTD and prevented excess reaction. The less reduction caused improvement in initial cycle efficiency. This improvement helps to make high energy density batteries.

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