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Effect of Sodium Chloride as Electrolyte Additive on the Performance of Mesocarbon Microbeads Electrode

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A low cost and environment benign salt of sodium chloride (NaCl) was used as an additive in low temperature electrolyte (Lithium hexafluorophosphate($LiPF_6$) / ethylene carbonate(EC) / propylene carbonate(PC) / ethyl methyl carbonate(EMC) (0.14/0.18/0.68, wt.)) to improve the electrochemical performance of mesocarbon microbeads(MCMB) anode. The initial Li extraction capacity of MCMB electrode was 304.8mAh g^{-1} in this electrolyte when the content of EC was remarkably reduced for a better conductivity. Whereas, a value of 357.6mAh g^{-1} was attained in the presence of NaCl additive. The electrochemical performance of MCMB was largely enhanced in the low temperature electrolyte with NaCl. The effect of NaCl additive on the electrode performance was examined by cyclic voltammetry(CV), electrochemical impedance spectroscopy(EIS), scanning electron microscopy(SEM) and X-ray photoelectron spectroscopic(XPS).

Keywords: low temperature electrolyte, sodium chloride, mesocarbon microbeads, lithium ion battery

1. INTRODUCTION

MCMB is widely applied as a good host material for lithium ion intercalation with its advantages of low working potential close to lithium metal, high specific capacity and low cost. At low temperature, the high electrochemical activities of anodes always make cathodes a limiting factor to battery performance. Much research on the low temperature application of lithium ion battery is performed on electrolyte optimization and cathode modification, whereas the compatibility between electrolytes and anodes (such as MCMB) is barely reported. PC and EMC are largely used at low temperature since they can improve electrolyte conductivity as co-solvents with EC. $LiPF_6$/EC/PC/EMC(0.14/0.18/0.68) has been used as a low temperature electrolyte with high conductivity at -40°C in our work. The high conductivity is attained by decreasing the content of EC to 0.14($W_{EC}/W_{solvents}$), which leads to an inferior film forming ability in this low temperature electrolyte because EC is essential to the formation of solid electrolyte interphase(SEI). It is needed to add film forming agents in the electrolyte to form the SEI film on the anode surface.

Various additives have been reported to be effective in electrode surface treatment, such as vinylene carbonate(VC) [1], CO_2 [2], polymers [3] and silicon-contained substances [4]. In addition, the effect of alkaline metal ion on graphite electrode was studied by Komaba group [5-8]. Uniform and smooth SEI film was formed on the electrode in 1mol L^{-1} $LiClO_4$/EC/DMC(1:1) electrolyte containing a small amount of $NaClO_4$ [6]. Only sodium ion was helpful in film forming while potassium ion was harmful as Komaba pointed out [9]. But Zheng et al [10] obtained an opposite result in which K^+ also showed positive effect. Komaba et al [5,7,8] also studied the pretreatment of graphite powder in the aqueous solution containing LiCl, NaCl, KCl or Na_2CO_3, found that the coating including alkaline metal ions on the graphite reduced the polarization of electrochemical reaction at the interface and increased the kinetic rate of lithium intercalation and deintercalation. But, the study is seldom noticed about the effect of NaCl as electrolyte additive on the performance of anodes, especially at low temperature. In the present work, the effect of NaCl on MCMB electrode is investigated as an additive in low temperature electrolyte, the cyclic performance of the electrode is examined as well.

2. EXPERIMENTAL

Solvents were used as received without further purification. NaCl,$NaPF_6$ and LiCl (all in 1 wt%, 99.9%, Aladdin Chemistry Co. Ltd, China) were added into 1mol L^{-1} $LiPF_6$/EC/PC/EMC (0.14/0.18/0.68) in an argon-filled glove box. NaCl was partly disolved with some particle precipitation in the electrolyte and the supernate was used in coin cells. The mass ratio of the disolved NaCl to the electrolyte is about 0.19%. In addition, 1 wt% $NaPF_6$ was totally dissolved in the electrolyte. LiCl suspensed in the electrolyte. For simplicity, 1% was still used in paper to denote the salts added cases. MCMB (Reshine New Materials Co., Ltd., China) powder was mixed with 5 wt.% super P and 10 wt.% polyvinylidene fluoride using 1-methyl-2-pyrrolidinone as a solvent to make viscous slurry. The slurry was coated on copper foil and then dried at 80°C for 20h under vacuum prior to assembly. CR2025 coin cells including MCMB/Li and MCMB/MCMB were fabricated in a glove box. The potentials herein were refered to Li^+/Li redox couple.

MCMB/Li cells were charged/discharged between 0.02-2.0V on CT2001A Land tester. The cells cycled for 6 times in the electrolytes with/without NaCl were disassembled in an argon-filled glove box to provide the cycled electrodes for symmetric cells used in EIS measurement. CV and EIS (100 Hz to 0.1 MHz, 5 mV perturbation) were tested on CHI660 analyzer. The cycled MCMB electrode (lithiated) was washed with pure EMC and then dried in vacuum before SEM (S-4800,) or XPS measurements. The XPS test was conducted on a PHI QUANTERA-II SXM system(Japan/Uivac-PHI, INC), using a monochromatised MgKα radiation source. The graphite peak at 248.3eV was used as a calibration reference for the final adjustment of the energy scale in the presented XPS spectra.

3. RESULTS AND DISCUSSION

The electrochemical activity of the electrode in the electrolyte containing NaCl is considerably superior compared to the additive free case according to the large current peak as shown in Fig.1. The reduction peak at 0.76V is visible in the inset Fig.(a), a small peak at 1.41V (inset Fig.(b)) appears in spite of a micro-level of the current. It is indicated that the addition of NaCl in the electrolyte has a positive impact on the electrochemical behavior of MCMB.

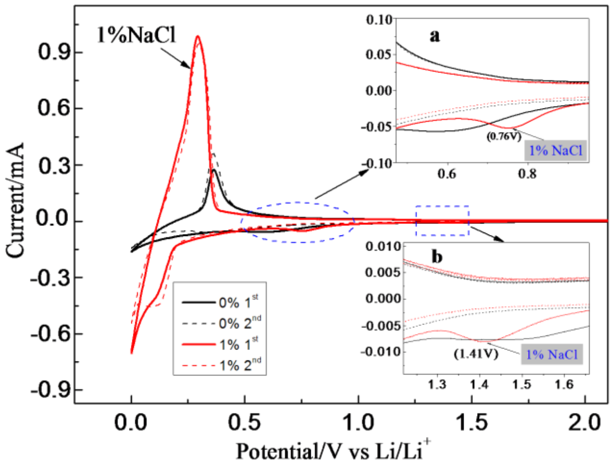

Figure 1. Cyclic voltammograms of fresh MCMB electrode in 1mol L^{-1} $LiPF_6$/EC/PC/EMC(0.14/0.18/0.68) with and without NaCl between 2.0V~0.0V at 0.1mV s^{-1}

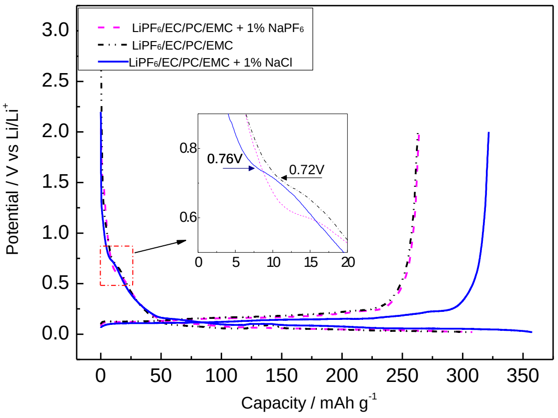

Figure 2. The discharge/charge curves of MCMB electrodes in electrolytes with/without NaCl or $NaPF_6$ at the first cycle (from open circuit potential to 0.02V and then to 2.0V, 19mA g^{-1})

Fig.2 shows the initial charge/discharge (corresponding to Li extraction/insertion) curves of MCMB electrode at a current density of 19mA g^{-1}(0.05C). The cathodic plateau from 0.16 to 0.02V, representing the characteristic reaction of Li insertion into the MCMB electrode, is ~40mV higher than the case of additive free, and the anodic plateau from 0.02 to 0.20V, meaning Li extraction, is ~40mV lower. It's worth noting that the small plateau at ~0.76V for NaCl addition in the inset of Fig.2, corresponding to the low reduction peak in Fig.1, is ~40mV higher than that of additive free(0.72V), too. So it is inferred that the reaction at 0.76V is the same with the one at 0.72V of additive free case while the two potentials for the same reaction are 40mV apart. This decrease of polarization may be attributed to a superior SEI film which accelerates Li^+ transfer through the interphase. Moreover, the initial discharge/charge capacities are 357.6mAh g^{-1}/321.7mAh g^{-1} in 1mol L^{-1} $LiPF_6$/EC/PC/EMC with NaCl, higher than 304.8mAh g^{-1}/262.8mAh g^{-1} (additive free), respectively. But, in comparison with the case of additive free, the addition of $NaPF_6$ doesn't make any capacity improvement (see Fig.2), which is not in agreement with the study of Komaba [6]. The result seems to indicate that separate Na^+ makes no contribution, and Cl^- also takes an important role in the electrolyte modification. Thus, LiCl may be a potential additive in the electrolyte for anode performance improvement. However, as verified in Fig.3, it is found that LiCl additive (nominally, 1wt.%)is extremely harmful to the cathode performance. While in the presence of NaCl additive, the cathode displays normal charge/discharge behavior, showing a good compatibility with the NaCl-added electrolyte. So it is attractive to study the modification of the low temperature electrolyte through using NaCl as additive.

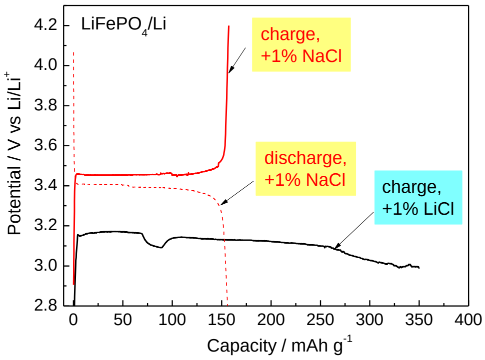

Figure 3. Charge/discharge curves of $LiFePO_4$ electrode in electrolytes with LiCl and NaCl. (room temperature, 0.1C)

Fig.4 shows the electrode morphologies in the electrolytes with/without NaCl. Compared to the fresh MCMB electrode with nothing on it (Fig.4(a)), the electrode soaked in $LiPF_6$/EC/PC/EMC (0.14/0.18/0.68) for 10 days without any cycling is covered with a thick film (Fig.4(b)). It may be ascribed to the decomposition products of solvents when the cell is stored at 2V. Whereas, it is suppressed in the low temperature electrolyte with NaCl additive, as can be seen in Fig.4(c), the film becomes apparently thin in the NaCl-added case. For the electrodes charged/discharged for 20 cycles, the film is more uniform and integrated in NaCl-added electrolyte than NaCl-free one (see Fig.4 (e) and Fig.4(d)). EIS investigation was performed to evaluate the SEI formed in different electrolytes. As the EIS data obtained from a two-electrode cell cover the individual impedances of cathode and anode

[11, 12], so symmetric cells were adopted in the measurement to get more reasonable results. The MCMB/MCMB cells were assembled with two cycled MCMB electrodes and filled with the same electrolyte of $LiPF_6$/EC/DMC (EC:DMC=1:1, wt%). The Nyquist plots are shown in Fig.5. The diameter of the first semi-circle corresponds to the impedance of the SEI film (R_{SEI}) on the two same electrodes in the symmetric cell, assuming a negligible contribution from the separator. So, the R_{SEI} of the MCMB electrode once cycled in the electrolyte with NaCl additive is 9.82Ω, calculated from the first semi-circle diameter. R_{SEI} exhibits to be 61.25Ω according to the value of 122.5Ω in the case of NaCl free, which is 6 times larger than its NaCl counterpart. Therefore, it’s concluded that the R_{SEI} of the MCMB electrode decreases in the presence of NaCl, which can facilitate the fast transfer of lithium ion through the SEI film. As a result, the reactivity of MCMB is enhanced, according with the analysis in CV results.

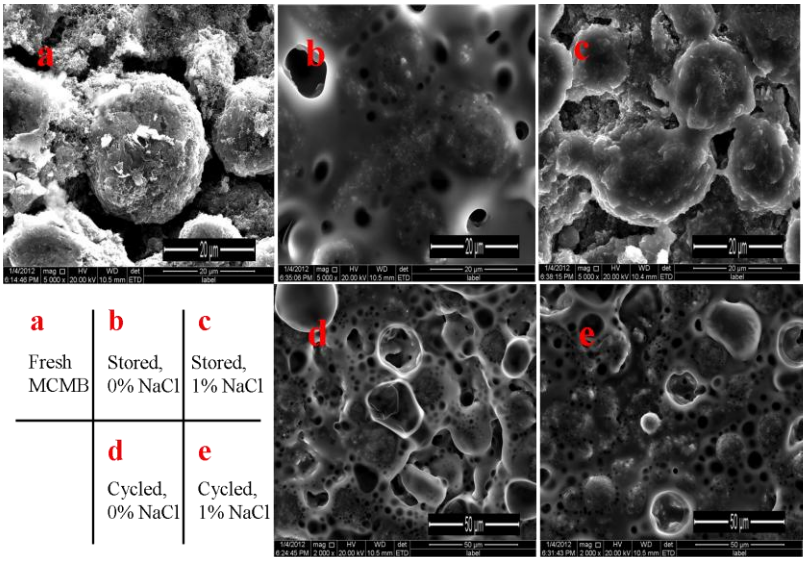

Figure 4. SEM images of MCMB electrodes (a, Fresh MCMB electrode, b and c, MCMB electrodes stored in NaCl-free and NaCl-added electrolytes for 10d without any cycling, d and e, MCMB electrodes charged/discharged for 20 cycles in NaCl-free and NaCl-added electrolytes, lithiated)

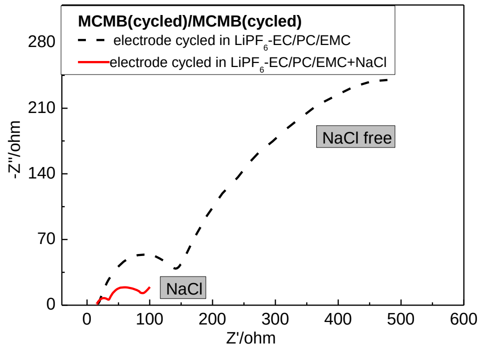

Figure 5. Nyquist plots for MCMB electrodes in the symmetric MCMB(cycled)/MCMB(cycled) cells

The XPS spectra of C1s, O1s, F1s, P2p and Li1s of MCMB electrodes cycled 20 times in the electrolytes with/without NaCl are presented in Fig.6 to examine the composition change on the surface of MCMB electrode. It's revealed that there is almost no change on elements except for the intensity of each peak. The intensities of peaks representing C-O, C=O, C-F, P-O, $Li_xPO_yF_z$, Li_xPF_y, Li_2CO_3 decrease in the presence of NaCl additive. Meanwhile, no peaks are found for elements Na and Cl in the XPS spectra (Fig.7), which means NaCl doesn't deposit or react with the electrolyte to form products on the MCMB surface. The phenomena also happen on the cathode $LiFePO_4$ in the electrolyte with NaCl additive. More efforts are needed to expatiate the role of NaCl additive further.

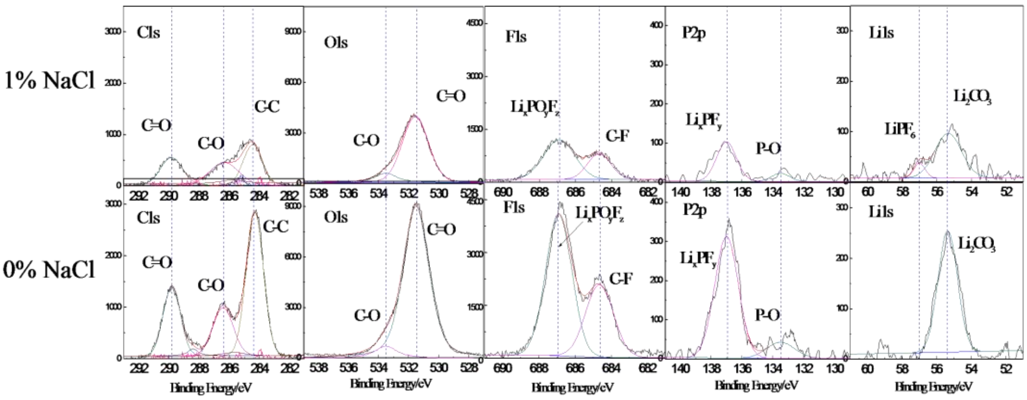

Figure 6. C1s, O1s, F1s, P2p and Li1s XPS spectra of MCMB electrodes (delithiated) cycled with NaCl(top) and without NaCl(bottom) electrolytes

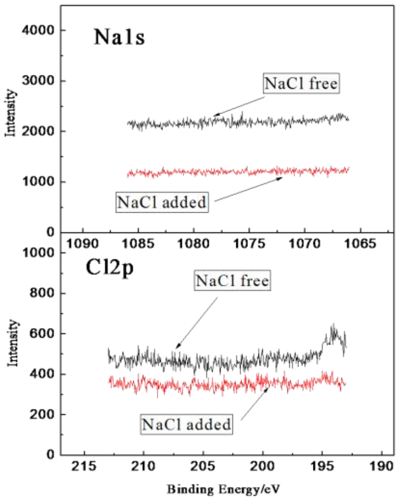

Figure 7. Na1s and Cl2p XPS spectra of MCMB electrodes (delithiated) cycled in the electrolytes with/without NaCl

Moreover, the MCMB electrode was charged/discharged cyclically to evaluate the effect of NaCl addition on its electrochemical performance, as shown in Fig.8(a). The Li extraction capacity of the electrode cycled in the low temperature electrolyte rapidly drops to 115.7mAh g^{-1} after 52 cycles at room temperature. However, the electrode performance is enhanced obviously in the presence of NaCl additive, a capacity value of 278.2 mAh g^{-1} is obtained after 52 cycles. Only 0.21% of the value is lost per cycle at the current density of 185mA g^{-1} compared to 1.14% loss in the NaCl-free case. The cycliability of MCMB is obviously enhanced with the NaCl addition in the electrolyte. The performance improvement also happens at -20°C in the NaCl-added case (Fig.8(b)). In a word, the compatibility of the MCMB electrode with the low temperature electrolyte is modified by the addition of NaCl, which extends the electrolyte application to a wider temperature range.

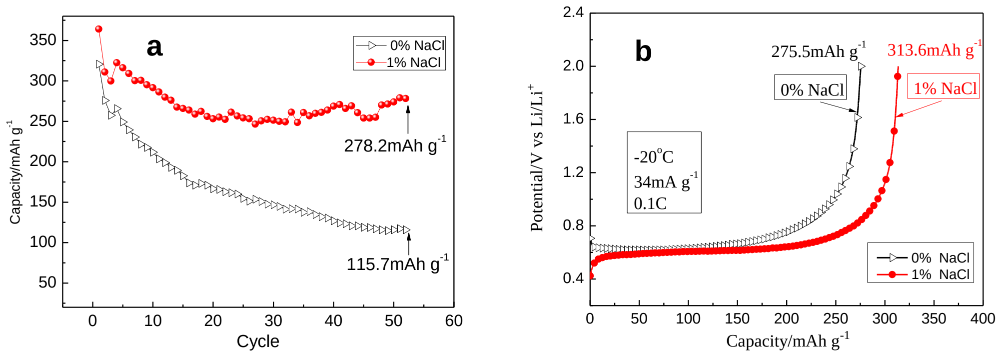

Figure 8. Discharge capacities (a, room temperature, 0.05C for the first cycle, 0.5C for the rest,) and -20°C charge curves (b, 0.1C(37mA g^{-1})) of MCMB electrodes in electrolytes with /without NaCl

4. CONCLUSIONS

The electrochemical performance of MCMB electrode is substantially enhanced in the low temperature electrolyte containing 0.19wt% NaCl. Li extraction capacity of 278.2mAh g^{-1} is attained for the electrode in NaCl-added electrolyte after 52 cycles (0.5C, 185mA g^{-1}), around 160mAh g^{-1} more than the value in the case of NaCl-free. The chemical species in the SEI film formed in the NaCl-added and NaCl-free electrolytes are qualitatively identical. But the SEI film in the NaCl-added case is more uniform and integrated, and its R_{SEI} is 9.82Ω, 6 times smaller than its NaCl-free counterpart. The decreased impedance of the SEI film is helpful for the performance improvement of the MCMB electrode. The compatibility of MCMB with the low temperature electrolyte is enhanced significantly by the NaCl addition irrespective of at low or room temperatures.

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