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Opposite influences of K$^+$ versus Na$^+$ ions as electrolyte additives on graphite electrode performance

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Abstract

Electrochemical performance of a graphite electrode for lithium ion batteries are easily improved by sodium ion dissolved in an electrolyte solution as reported recently by our group. On the contrary, when potassium ions were added by dissolving $0.2\,\mathrm{mol\,dm^{-3}}$ KPF$_6$ into a $1\,\mathrm{mol\,dm^{-3}}$ LiPF$_6$ ethylene carbonate–diethyl carbonate (1:1, v/v) electrolyte solution prior to charge–discharge cycle, an electrochemical performance of a graphite electrode was deteriorated compared to that tested in an additive free electrolyte; larger irreversible capacity at the first cycle and worse retention of discharge capacities on successive cyclings. During the first charge in a potassium additive system, ex situ XRD observation of graphite electrodes revealed that lithium intercalation hardly proceeded in the lower potential region less than 0.1 V versus Li though lithium ions were intercalated at >0.1 V. Electroreduction of potassium ions on the electrode occurred instead of lithium intercalation into graphite in the lower potential region. Furthermore, the electrode surface morphology observed by electron microscopes after charge–discharge tests got less uniform in the potassium added electrolyte.
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1. Introduction

Graphite electrode is favored for Li ion battery application because it exhibits a high specific capacity, low working voltage closed to lithium metal and superior cycling behavior. However, a graphite anode shows a relatively large irreversibility only at the first cycle, because reductive decomposition of an electrolyte solution occurred at the graphite surface during the first charging (electrochemical reduction) including the formation of solid electrolyte interface (SEI).

As the existence of SEI layer plays an important role in reversible lithium intercalation into interspace between graphene layers, chemical modification of graphite surface including an SEI film has attracted wide attention to improve battery performances. In order to modify and improve the SEI film, several additives dissolved into an electrolyte solution have been successfully found to be effective: such as vinylene carbonate [1], HF [2] and CO$_2$ [3–5]. Previously, we emphasized that an electrochemical performance of a negative carbon electrode was dramatically influenced by inorganic electrolyte additives such as (transition) metal ions [6,7] and ammonium iodide [8]. Furthermore, we recently described the new approach to enhance the graphite anode performances based on the addition of a small amount of a sodium salt in an electrolyte solution [9]. As reported by Tossici et al., potassium intercalated graphite (KC$_8$) prepared by chemical reaction was able to be employed as a high-rate negative electrode for rechargeable lithium ion batteries [10–12] because of the formation of an insoluble protective KClO$_4$ layer on the surface [13], however, there is no report on a graphite electrode performance in an electrolyte containing both lithium and potassium salts to the best of our knowledge. Here we report the comparative study on influences of Na$^+$ and K$^+$ ions

as an electrolyte additive on a negative graphite electrode for Li ion batteries, which were oppositely resulted from their different electrochemical reactivity.

2. Experimental details

Reagent grade natural graphite (Nakarai Tesque, Inc., average particle size 10 μm) and potassium hexafluorophosphate were used. Battery grade lithium foil, ethylene carbonate (EC), diethyl carbonate (DEC) and $LiPF_6$ were used without any further purification. Potassium hexafluorophosphate was dried in vacuum at 100 °C for >1 day to remove residual water prior to its use in the electrochemical cell. The electrolyte used was a $1 \, mol \, dm^{-3}$ $LiPF_6$ containing EC–DEC (1:1, v/v) solution and potassium ion was added by dissolving KPF_6 into the electrolyte solution before electrochemical cell assembly. In order to eliminate a dependence of anion species on graphite electrodes, the same potassium salt to lithium one was used as an additive. Although the sodium system was investigated by using perchlorates in our previous work [9], potassium/lithium hexafluorophosphates were used for a potassium added system because of very low solubility of $KClO_4$ in EC–DEC solution similarly to the previous observation that $KClO_4$ is insoluble in $LiClO_4$ EC–dimethyl carbonate solution [13].

Detailed conditions of the electrochemical measurements are described in our previous paper [6,9]. Mixture of the graphite (whose weight was between 5 and 10 mg) and poly(vinylidene fluoride) in a weight ratio of 9:1 was used for preparation of the working electrode. Li foils were used for both the reference and counter electrodes. Constant charge (lithium intercalation) and discharge (lithium deintercalation) currents of 70 and $350 \, mA \, g^{-1}$ were applied to the electrode and they were cycled between 0.00 and 2.0 V versus Li/Li^+ at room temperature (25 ± 2 °C) in a glove-box under an argon atmosphere (dew point < −80 °C).

Surface morphology of an electrode was observed with scanning electron microscopy (SEM; Hitachi S-2250NII). To observe the graphite after electrochemical cycling, graphite electrode was quickly transferred from an electrochemical cell to SEM observation chamber after washing with pure EC–DEC and drying in vacuum. Ex situ X-ray diffraction was employed using a plastic-wrapped electrode to avoid exposing the electrochemically tested electrode to an atmosphere.

3. Results and discussion

By adding Na^+ ions into an electrolyte, the irreversible capacity is reduced and a higher reversible capacity is obtained with no significant difference in the potential variation corresponding to the staging structures of lithium intercalation–deintercalation into/from natural graphite in the potential region less than 0.3 V in spite of sodium addition [9]. The sodium ion addition hardly modified the bulk properties of the electrode and electrolyte, however, contributed to reduce the influence of a surface film including SEI on the electrochemical kinetics. In order to compare influences of alkaline metal ions on the negative electrode of lithium ion batteries, we here chose potassium, which is another neighboring alkaline metal element to sodium in the periodic table.

Fig. 1 shows the 1st and 50th charge–discharge curves of a graphite electrode obtained at a current density of $70 \, mA \, g^{-1}$ in $1 \, mol \, dm^{-3}$ $LiPF_6$ in EC–DEC without and with $0.2 \, mol \, dm^{-3}$ KPF_6. In an additive free medium, the natural graphite showed a reversible capacity of $339 \, mAh \, g^{-1}$, and an irreversible capacity of $65 \, mAh \, g^{-1}$ was observed due to the well known electroreductive formation of the SEI on graphite around 0.8–0.3 V [14,15]. On the other hand, in the case of a K^+ added electrolyte, the irreversible capacity increased up to $76 \, mAh \, g^{-1}$, and a lower reversible capacity of $322 \, mAh \, g^{-1}$ was obtained. It seems that no significant difference in the potential variation corresponding to the stage structures of lithium intercalation–deintercalation in the whole potential region in spite of potassium addition.

The variation in discharge capacities of a graphite negative electrode with and without K^+ addition during cycling was greatly different as plotted in Fig. 2. At the first cycle examined at 70 and $350 \, mA \, g^{-1}$, the reversible capacities for
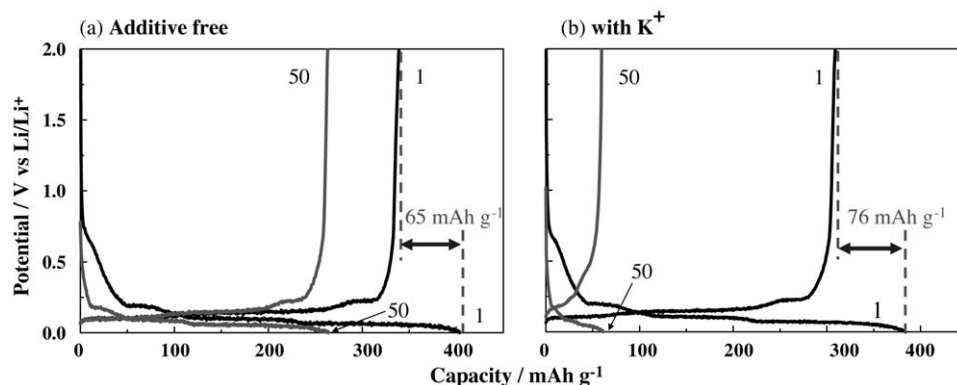

Fig. 1. Charge–discharge curves of graphite negative electrodes in (a) additive free and (b) $0.2 \, mol \, dm^{-3}$ KPF_6 added EC–DEC (1:1) electrolyte containing $1 \, mol \, dm^{-3}$ $LiPF_6$ at $70 \, mA \, g^{-1}$.
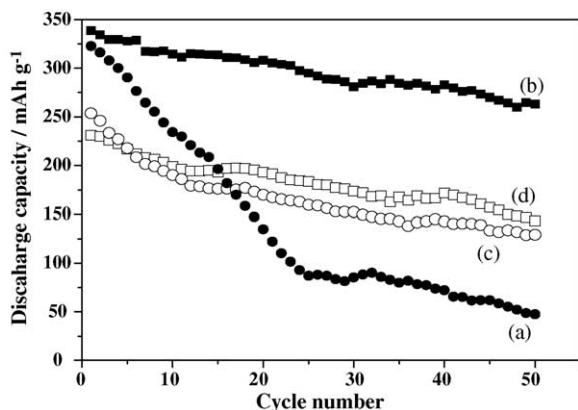
Fig. 2. Discharge capacities vs. cycle number plots of graphite electrodes (a) with and (b) without KPF_6 at 70 mA g^{-1}, and (c) with and (d) without KPF_6 at 350 mA g^{-1}. Electrolyte: 1 mol dm^{-3} $LiPF_6$/EC–DEC (1:1).

a potassium ion added electrolyte are similar to those of additive free one. However, the discharge capacity was faded more rapidly by dissolving KPF_6, especially; the discharge capacity after 50 cycles was less than 50 mAh g^{-1} when the lower current was applied for cycling test. In the 50th potential variation curves as shown in Fig. 1, there hardly appeared typical plateaux corresponding to the Li intercalated stages in a K$^+$ ion added electrolyte even though the plateaux were clearly observed after 50 cycles in an additive-free electrolyte. The addition of K$^+$ ions into an electrolyte was unfavorable to battery performance of a graphite anode, depending on charge–discharge rate. Consequently, we observed a negative effect of K$^+$ ion addition despite the positive effect of a sodium additive.

In order to investigate electrochemical reactions in a potassium added electrolyte, cyclic voltammograms were compared in additive-free and potassium added electrolytes at the first cycle as shown in Fig. 3. As expected from the galvanostatic charge–discharge tests, this voltammetry confirmed that electrochemical activity of graphite was decreased by potassium addition because of lower oxidative/reductive current densities in cathodic and anodic scans, respectively. At least,
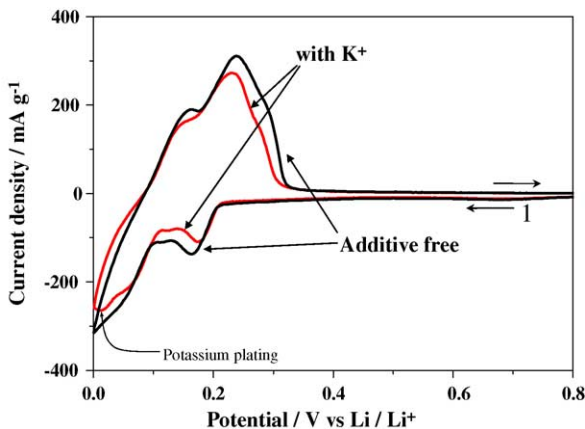
two redox couples are clearly observed in both systems between 0.3 and 0.1 V which should be due to staging of lithium intercalated graphite, and potential difference between oxidative and reductive peaks in the two redox couples are reduced by adding potassium into an electrolyte. As mentioned below (in Fig. 4), potassium ions might be slightly intercalated into graphite in the initial charging, resulting in the expansion of interlayer distance by larger size of potassium ion than that of lithium ion. As a result, polarization is reduced by lower resistance due to enhanced Li diffusion in the interlayer space. For the potassium adding system, an additional reductive peak appears around 10 mV versus Li. From Nernstian equation, equilibrium potential of potassium deposition, E_{K/K^+}, at 25 °C should be estimated as follows [17] when activity of potassium, a_{K^+}, is assumed to be 0.2:

$$E_{K/K^+} = E^0_{K/K^+} + 0.059 \log a_{K^+} = -2.924 - (-3.045)$$
$$+ 0.059 \log 0.2 = 0.080 \ [V \ \text{versus} \ Li/Li^+]$$

where the E^0_{K/K^+} is standard electrode potential of K/K$^+$ couple. As the additional reductive peak was observed below E_{K/K^+}, it might be due to deposition of potassium metal on the electrode surface at the end of charging. From these results, electrochemical intercalation of lithium ions would predominantly occur over that of potassium ions due to the larger size (1.5 Å [16]) and lower concentration (0.2 mol dm^{-3}) of potassium ion than those (0.9 Å [16] and 1 mol dm^{-3}, respectively) of lithium ion. Furthermore, the variation in graphite electrode structures was investigated by ex situ XRD technique.

Fig. 4 shows ex situ XRD patterns of graphite electrodes galvanostatically electroreduced (charged) to 2.0, 0.2, 0.1 and 0.0 V in additive free and potassium added electrolytes followed by equilibrating the electrode potential for several hours in a cell. In the diffractograms, the intense diffraction lines of 0 0 l clearly appeared at $2\theta = 23$–$27°$, and d spacing values estimated from the strongest diffraction peaks were inserted in each pattern of Fig. 4. Since 0 0 l peaks shifted toward lower angle with decreasing the charging potentials, electrochemical intercalation occurred into the space between graphene layers. However, the variation in d values of the 0 0 l peaks in an additive free electrolyte was different from that in a K$^+$ added one. After charging to 2.0 V, the interlayer space is identical to that of graphite because of no apparent electrochemical reaction. When the electrode was charged to 0.2 V, d values were slightly increased by adding K$^+$ ions, that is, the difference was 3 pm (=0.337–0.334 nm). As described by Tossici et al. [10,11], small (residual) amount of potassium derived from KC_8 in a lithium-containing electrolyte expanded the graphite structure even if potassium ions were removed from KC_8 compared with that of pure graphite. It is like that the lower polarization of redox couples in cyclic voltammograms in Fig. 3 was due to the slight interlayer expansion by adding potassium ion into an electrolyte which favored the simultaneous and/or subsequent lithium intercalation–deintercalation process accompanied with
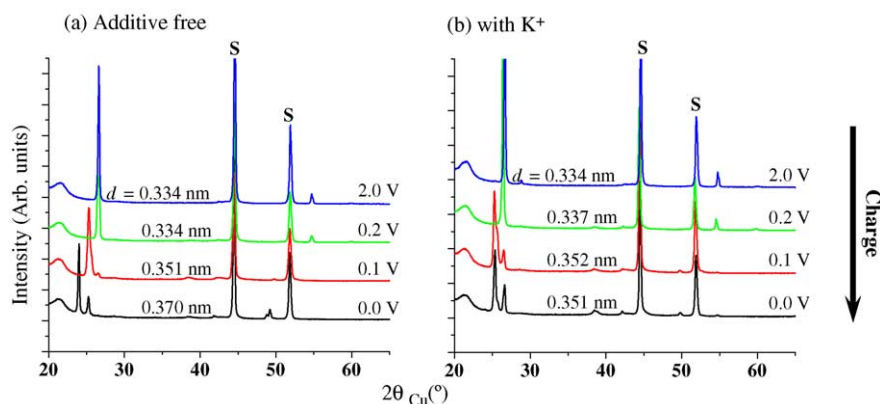

Fig. 3. Cyclic voltammograms of graphite electrodes with and without KPF_6 at 0.5 mV s^{-1}. Electrolyte: 1 mol dm^{-3} $LiPF_6$/EC–DEC (1:1).

Fig. 4. Ex situ XRD patterns of graphite electrodes during the initial charge in 1 mol dm^{-3} LiPF$_6$/EC–DEC (1:1) (a) without and (b) with KPF$_6$. Galvanostatic charging at 70 mA g^{-1} was stopped at 2.0, 0.2, 0.1 and 0.0 V vs. Li, and then the electrode was recovered for XRD measurement. S: current corrector (Ni).

enhancement of its kinetics. In consideration of the less expansion (3 pm) compared to the K-deintercalated graphite (6 pm [11]), a graphite electrode predominantly underwent lithium intercalation in a potassium added electrolyte at >0.1 V because of the larger size and the lower concentration of potassium ion.

Although the interlayer distances at 0.1 V were almost independent of the potassium addition, the fully charged electrodes possessed different d spacings. Values of d spacing increased from 0.351 to 0.370 nm in an additive free system which is close to $d_{0\,0\,2} = 0.372$ nm for LiC$_6$ [9,18]; however, almost constant d spacing was observed in K$^+$ added system suggesting no intercalation between 0.1 and 0.0 V during the initial charge. If potassium and/or lithium ions (co-)intercalated into graphite, the interlayer space should increase with increasing quantity of charge passed; additionally, a larger $d_{0\,0\,l}$ value than that in additive free at 0.0 V should be observed in case of K (co-)intercalated graphite such as 0.372 and 0.536 nm for LiC$_6$ and KC$_8$ [9,11,18], respectively, because of larger ionic radius of K$^+$ ion. As mentioned in Fig. 3, electroplating of metallic potassium around 10 mV occurred instead of lithium intercalation; thus, metallic potassium might obstruct graphite surface to prevent lithium intercalation into graphite less than 0.1 V. It is well

consistent with the almost same interlayer spaces at 0.1 and 0.0 V. Any diffraction peaks of K metal are not observed in ex situ XRD patterns. It might be due to low crystalline potassium or decomposition of highly reactive potassium metal with organic electrolyte solution in a cell and/or during sample preparation for ex situ XRD.

These results suggested that potassium plating cannot be prevented by the SEI layer formed between 0.3 and 0.8 V in a KPF$_6$ dissolved electrolyte and the graphite electrode suffers from deposition of potassium during every charging. Indeed, the surface of electrode after successive cycles was greatly different as shown in Fig. 5. In case of additive free, flake shape of pristine graphite is clearly distinguishable with more uniform and flat surface; however, potassium addition caused many deposits on electrode surface. Formation of many deposits was associated with repeating electrochemical deposition/dissolution of potassium. It is probable that the by-product between K metal and organic electrolyte was gradually accumulated on cycling resulting in capacity fading as seen in Fig. 2.

The Na$^+$ additive clearly enhanced the cycle performances of graphite and sodium component was detected at the surface, which is similar to our carbonaceous material prepared from molten carbonates [19]. This enhancement came from
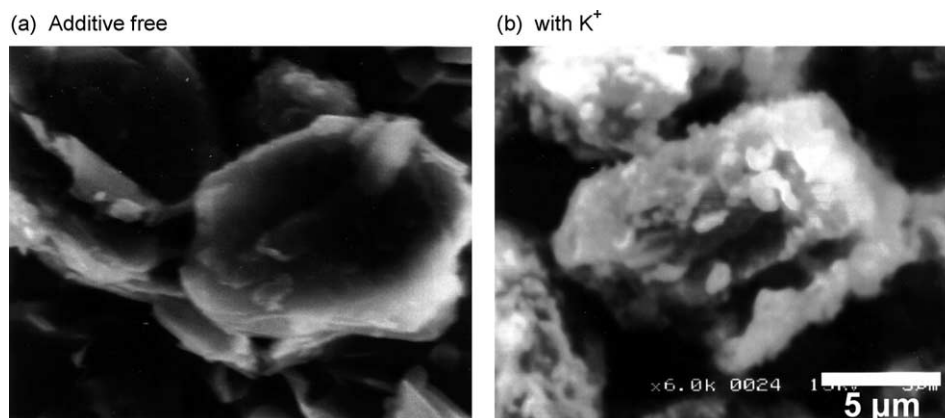

Fig. 5. SEM images of graphite electrode surfaces after 50 cycles in 1 mol dm^{-3} LiPF$_6$/EC–DEC (1:1) (a) without and (b) with KPF$_6$.

changing the SEI structure including the morphology, the composition and the impedance; furthermore, sodium ion did not participate in the reversible electrochemical reaction [9]. On the other hand, it was found that the K^+ additive had a disappointing influence on the graphite electrode performance though the intercalated potassium somewhat expanded graphite structure along c-axis to improve the kinetics of lithium intercalation at higher potential region than 0.1 V. Consequently, the addition of alkaline metal ions such as Na^+ and K^+ has the different influence on the electrochemistry of graphite electrode in lithium salt containing electrolytes which is due to their different electrochemical behaviors at the surface. As known generally, sodium intercalation into graphite occurred under very limited conditions compared to those of other alkali metals [20]. The enhancement by Na^+ addition is considered as one of the particular behaviors of Na^+, that is, no intercalation and no electrodeposition of Na metal but positive modification of SEI layer. However, potassium component in an electrolyte did take part in electrochemical deposition/dissolution and intercalation resulting in negative modification of a graphite anode.

Acknowledgements

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