Potassium Intercalation into Graphite to Realize High-Voltage/Power Potassium-Ion Batteries and Potassium-Ion Capacitors

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Abstract

Highly reversible potassium intercalation into graphite in carbonate ester solution at room temperature is achieved by electrochemical reduction at the potential approaching to K^+/K standard potential which is lower than that of Li^+/Li . The intercalation results in formation of stage-1 KC_8 compound with delivering 244 mAh g^{-1} of reversible capacity. The initial irreversible capacity is suppressed by polycarboxylate binder compared to poly(vinylidene fluoride) binder. The lower potential, good cyclability, and excellent rate capability are first demonstrated for energy storage applications. Because of the lowest potential and weakest solvation among Li^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} ion carriers, potassium shuttlecock mechanism between two insertion materials as “potassium-ion battery” is advantageous for higher-voltage/-power rechargeable batteries. The excellent rate performance is beneficial for the application to hybrid-type capacitor, “potassium-ion capacitor,” as an alternative to lithium-ion capacitors.

Keywords:potassium; intercalation;graphite; binder; potassium-ion battery; potassium-ion capacitor

Introduction

Lithium is broadly believed to be the best alkali metal element for high energy density batteries in terms of the lightest atomic weight and lowest standard potential among alkali metals. Lithium-ion batteries have been sophisticated as commercial rechargeable batteries for portable devices and transportation applications since 1991. In spite of the significant progress in lithium-ion technology, its available reserve is unevenly distributed especially in South America, most of countries should therefore depend on the import of lithium resource. Because of unlimited availability of sodium which is the second lightest alkali, sodium-ion batteries made from earth-abundant elements without toxic elements attract significant attention to realize affordable rechargeable batteries which can store high energy density comparable to lithium-ion batteries.¹

In Table 1, lithium, sodium, and potassium are compared as ionic carriers for non-aqueous rechargeable batteries. Because their ionic size plays a critical role in crystallization of insertion materials, especially for positive electrode, we are experiencing wider variety of Na-ion materials than Li-ion ones, due to significant difference of ionic size between sodium and lithium.² Furthermore, the atomic weight ratios of sodium and potassium against lithium are 3.3 ($=23/6.9$) and 5.7 ($=39/6.9$), respectively, which convinces us of no chance of sodium- and potassium-based

batteries. However, this comparison is fairly misleading to understand battery weight because pure alkali metals are never acceptable for consumer use due to safety issues. Actually, we should compare formula weight of positive electrode materials to consider their gravimetric capacity. For instance, the formula weight ratio of (P2-type $\text{Na}_{2/3}\text{CoO}_2$)/ LiCoO_2 is only 1.08, meaning only 8% weight gain of positive active material in entire Na-ion system. In case of potassium, the ratio of (P2-type $\text{K}_{2/3}\text{CoO}_2$)/ LiCoO_2 is 1.19, in spite of 5.7 times heavier potassium atom. This means that atomic weight of alkali does not remarkably affect total weight of batteries.

We note that battery's voltage is very important to realize high-energy density, since energy density (Wh) is determined by multiplying capacity (Ah) by average discharge voltage. A state-of-the-art lithium-ion battery is charged up to 4.4 V vs. Li, which is limited by anodic decomposition of electrolyte solution resulting in gas evolution. From the same reason, the charge cut-off voltage must be limited to ca. 4.1 V vs. Na, inevitably resulting in lower energy density than Li-ion. However, the standard potential of potassium is low in voltage ca. 0.1 V than that of lithium in propylene carbonate (PC) as seen in Table 1.³ As reported by Aurbach and coworkers,⁴ the surface film formed in potassium salt PC solution is more stable than that of sodium. A few potassium insertion materials for positive electrode were reported, e.g. Prussian blue thin film,⁵ FeSO_4F ⁶ and amorphous FePO_4 .⁷ Potassium can be intercalated into graphite to form KC_8 with a stage-1 structure by liquid-phase chemical reaction at ambient temperatures.⁸ These facts motivated us to realize graphite negative electrode for 4 volt class K-ion battery (KIB) and K-ion capacitor (KIC) as we succeeded in 3 volt Na-ion batteries based on Li-ion experiences. In this study, we investigate the electrochemical

potassium intercalation into graphite and demonstrate attractive redox performance for negative electrodes of non-aqueous potassium-ion batteries and capacitors.

Experimental

Natural graphite (particle size 3 μm) was mixed with binder, sodium polyacrylate (PANA), sodium carboxymethylcellulose (CMCNa), or poly(vinylidene fluoride) (PVDF) binders in weight ratio of 90:10 in adequate solvent of deionized water or *N*-methylpyrrolidinone. Details of graphite and binders are described in our previous paper.⁹ The resulting slurry was uniformly pasted onto aluminium foil or copper foil by doctor blade method, and then carefully dried at 150 °C for 12 h in a vacuum prior to cell assembly. The loading on the foils was ca. 0.8-1.0 mg cm⁻². Galvanostatic charge-discharge test (between 0.0 and 2.0 V vs. K⁺/K⁻ at ± 25 mA g⁻¹) and cyclic voltammetry were conducted in a coin-type K cell and three-compartment beaker-type cell,¹⁰ respectively. All the cells were assembled in Ar-filled glove box with satisfactory lower dew point below -80 °C. We handle potassium metal with special care through all experimental works.

Electrolyte solution used in this study was 1.0 mol dm⁻³ KN(SO₂F)₂ (potassium bis(fluorosulfonyl)imide, KFSI) or 0.5 mol dm⁻³ KPF₆ dissolved in ethylene carbonate (EC):diethyl carbonate (DEC) in a 1:1 (v/v) mixture. KFSI (Kanto Chemical), potassium metal, KPF₆ (Sigma-Aldrich), LiFSI (Kishida Chemical), NaFSI (Mitsubishi Materials), EC, DEC, PC, and Li- and Na-ion electrolyte solutions (battery grade, Kishida Chemical) were used as received without air exposure. Ex situ X-ray diffraction

(XRD) was conducted for tested electrodes washed with EC:DEC and then DEC.

Results and discussion

In order to examine potassium plating, cyclic voltammetry is conducted for nickel mesh as working electrodes because of no Ni-K alloying at room temperature. In Figure 1, potassium plating/stripping located at -0.15 V vs. Li^+/Li was observed in $0.5 \text{ mol dm}^{-3} \text{ KPF}_6\text{EC:DEC}$. The reason why $0.5 \text{ mol dm}^{-3} \text{ KPF}_6 \text{ EC:DEC}$ was used is the facts that $1 \text{ mol dm}^{-3} \text{ KPF}_6$ was not completely dissolved into EC:DEC, resulting in white-coloured dispersion, which may be similar to the condition of low purity NaPF_6 ¹¹, and in addition KClO_4 and KBF_4 were hardly soluble in EC:DEC and PC in our preliminary test. From Nernst equation, the standard potential of K^+/K is calculated to be -0.12 V vs. Li^+/Li , which agrees with the previous data of -0.09 V calculated for PC shown in Table 1.³ Clearly, reversible potassium deposition was observed without any electrolyte additives, such as fluoroethylene carbonate and vinylene carbonate,¹² which is probably due to passivation of potassium metal completed by electrolyte decomposition¹³ with low contamination level.¹⁴ The cyclic voltammogram reveals that potassium plating/stripping occurs at lower potential, which is highly advantageous for higher-energy density design.

The incomplete dissolution of KPF_6 powder results in the white dispersion, in addition, KClO_4 and KBF_4 are almost insoluble in PC. Consequently, we selected and used the only transparent and colorless liquid of $1 \text{ mol dm}^{-3} \text{ KFSI}$, which can be completely dissolved into EC:DEC, in our tests. Figure 1 compares the redox

properties of graphite electrodes in three different alkali cells. Sodium polyacrylate is selected as the binder to improve the solid electrolyte interphase (SEI)-passivation.¹⁵ In Li cells, the graphite delivers high reversible capacity of ca. 369 mAh g⁻¹ with high initial efficiency to form LiC₆ showing 372 mAh g⁻¹.¹⁰ The graphite showed no sodiation activity in the NaPF₆/EC:DEC solution as known generally.^{14a, 16} In case of potassium, the high capacity of 244 mAh g⁻¹ in 0 - 0.3 V is demonstrated, which corresponds to 87% of the calculated capacity of 279 mAh g⁻¹ based on KC₈ reversible formation by electrochemical reaction. Figure 1 further confirms the same electrochemical property when we used Al and Cu current collectors in K cells, which is consistent of no intermetallic phase of Cu-K¹⁷ and Al-K¹⁸ at room temperature. Adopting Al foil will be beneficial to practical KIB and KIC as a consequence of its lower cost and lighter weight than Cu which is necessary for lithium-ion counterparts.

Ex-situ XRD was conducted to identify the reversible redox reaction without air exposure for avoiding oxidative decomposition of KC₈.¹⁹ Figure 2 reveals phase transition from graphite to stage-one intercalation compound, KC₈ (ICSD #70020), of which the interlayer distance is ca. 5.3 Å,²⁰ by the electrochemical reduction. Because it returns to graphite after electrooxidation, potassium ions are reversibly deintercalated in the topotactic manner. From the diffraction lines of graphite and KC₈, the interlayer distance increases upon potassium intercalation from 3.36 and 5.2 Å, indicating 1.5 times increase in the distance, which is much significant than that of LiC₆ due to the larger ionic size than that of lithium. As stepwise potential variation appears for the K//graphite cell in Figure 1, phase transition including formation of different stage compounds, such as KC₂₄, is under investigation.

Figure 3 compares cycle performance of graphite with different binders. The reversible capacity, reversibility, and redox potential of the intercalation are basically identical for PVDF, PANa and CMCNa, except reversibility at the first cycle. Namely the irreversibility is due to SEI formation like lithium and sodium cases,^{14a} and the initial efficiency is improved by PANa and CMCNa compared to PVDF, as indicated in the figure. This improvement should be attributed to the pre-formed SEI effect of PANa²¹ and CMCNa,²¹ and in addition, to the suppressed defluorination of PVDF.²¹ Though the interlayer distance is expanded 50% upon electrochemical potassium intercalation, the volume expansion results in no capacity degradation during >50 cycles for PANa, which is likely due to its surface coatability and higher mechanical strength of composite electrodes.^{9c} Surface analyses of the graphite electrode are in progress and will be reported elsewhere.

To further examine discharge rate-capability as KIB or KIC, the PANa electrode was charged (potassiated) at a low current of C/10 and then discharged (depotassiated) at different rates as shown in Figure 3d. Surprisingly, capacity loss is hardly observed at 15C rate despite the polarization of approximately 0.6 V. Note that the polarization includes 0.5 V potassium stripping polarization at the counter K electrode in coin-type cell, which was estimated in three-electrode configuration test at the same condition. Therefore, the actual polarization of graphite electrode is mostly only 0.1 V, which is quite small compared with typical lithium and sodium insertion/de-insertion at carbonaceous electrodes. This is consistent with a recent paper describing that alkali diffusivity is higher for KC₈ than those for lithiated and

sodiated graphites at room temperature.²² Additionally, as Al anodic corrosion does not occur in high purity LiFSI EC:EMC electrolyte but is induced by LiCl impurity in low purity LiFSI,²³ KFSI electrolyte is expected to have no damage for Al used for positive electrode.

Generally, K^+ ions have much weaker Lewis acidity among the alkalis, which is important for ion transfer in electrolyte and at electrode/electrolyte interface.²⁴ This causes smaller Stoke's radius of solvated ions, which should lead to larger transport number and higher mobility for K^+ . Indeed, our measurement reveals that ionic conductivity at ambient temperature is found to be 9.3, 9.7 and 10.7 $mS\ cm^{-1}$ for 1 $mol\ dm^{-3}$ LiFSI, NaFSI, and KFSI EC:DEC, respectively, indicating the highest conductivity of K system. This superior character of K^+ ions is well known as KOH aqueous solution practically used in alkaline batteries. Safety issue must be taken into account because potassium metal is violently reactive compared to Li and Na metals. It is noticed that its melting point, 64°C, is much lower than others listed in Table 1. If dendrite deposition by overcharging KIBs induces the internal short-circuit inside KIB, the dendrite is heated by Joule heat, and then the heat will swiftly fuse the dendrite which avoids the thermal runaway of KIB.

By realizing graphite negative electrode for KIB and KIC, novel field of materials science of potassium insertion materials, binders, salts, organic solvents, additives, solid electrolyte etc. will attract us to next generation battery and hybrid-capacitor beyond Li-ion and Na-ion.

Conclusions

This study demonstrates the graphite-polyacrylate electrode for higher-voltage and -power KIB/KIC operable at room temperature. Although potassium atom is heavier than lithium and sodium ones, promising battery performance is highly expected by future study.

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Figure 1. (upper) Cyclic voltammograms of Ni mesh electrode in $0.5 \text{ mol dm}^{-3} \text{ KPF}_6$ EC:DEC at 0.05 mV s^{-1} in beaker-type cell equipped with Li^+/Li reference electrode. (bottom) Charge-discharge curves of graphite electrode with polyacrylate binder in (a) $1 \text{ mol dm}^{-3} \text{ LiPF}_6$ EC:DMC of Li cell, (b) NaPF_6 EC:DEC of Na cell, and (c,d) $1 \text{ mol dm}^{-3} \text{ KFSI}$ EC:DEC of K cell. Graphite composite electrode was formed on (a,c) Cu and (b,d) Al foils.

Figure 2. Ex-situ XRD patterns of graphite-PANa electrode: (a) as prepared, (b) after first reduction at 0.0 V , and (c) after oxidation 2.0 V in K cells.

Figure 3. Charge-discharge curves of graphite electrode formed on Al foil with (a) PVDF, (b) PANa, and (c) CMC binders in $1 \text{ mol dm}^{-3} \text{ KFSI}$ EC:DEC of K cells, and (d) oxidation-rate capability for the PANa electrode.

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Table 1. Comparison of alkali metals' characters as an ionic carrier of non-aqueous rechargeable batteries.

A =	Lithium	Sodium	Potassium
Abundance	+	+++++	+++++
Relative atomic mass / -	6.9	23	39
Shannon's ionic radii of A ⁺ / Å	0.76	1.0	1.4
Melting point / °C	179	98	64
E° (A ⁺ _{aq} /A) / V vs. SHE*	-3.040	-2.714	-2.936
E° (A ⁺ _{PC} /A) / V vs. SHE*	-2.79	-2.56	-2.88
E° (A ⁺ _{aq} /A) / V vs. Li ⁺ _{aq} /Li*	0	0.326	0.104
E° (A ⁺ _{PC} /A) / V vs. Li ⁺ _{PC} /Li*	0	0.23	-0.09

* The standard electrode potentials at 279.15 K are calculated from standard molar Gibbs energy of hydrated and PC-solvated A⁺ ions. Ref.) Marcus, Y., *Pure Appl. Chem.*, **1985**, 57, 1129.