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ABSTRACT

CaB₆ has a tunneled framework lattice structure that is suitable for intercalation of ions. Electrochemical charge-discharge testing of CaB₆ in lithium containing non-aqueous electrolyte showed a specific capacitance of 35.7 F/g at 0.42 A/g current rating. Even though the specific capacitance was low, CaB₆ shows promise as a Li-ion intercalating material because of its higher diffusivity (3×10^{-10} cm²/s), p-type semiconductivity, high conductivity, and low density.

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1. Introduction

Calcium hexaboride has attracted a wide spread attention because of its ferromagnetic properties when dilute doped with La and Ba [1]. The first principle calculations based on local density approximation indicated that CaB₆ could be a semimetal [2]. Wu et al. predicted CaB₆ to be a semiconductor with a band gap of 0.3 eV using the weighted density approximation [3]. On the other hand, *sX-LDA* based calculations performed by Lee et al. indicated a wider band gap of 0.89 eV which was supported by calculations of other researchers [4,5]. The conduction band of CaB₆ predominantly consists of B 2*p* and Ca 3*d*, and the valence band is constituted by B 2*p* and B 2*s* orbitals. The semiconductivity of CaB₆ was considered to be n-type when the material was having Ca vacancies [6]. Kang and Park attributed the n-type semiconductivity to the presence of antisite B atoms that formed B₇ covalent structure and acted as donor-like defects in the CaB₆ [7]. The first principles calculations of Kang and Park indicated that point defects such as Ca vacancies, B₆ vacancies, Ca-antisites, and B vacancies predominantly acted as deep level acceptors and possibly rendered the material a p-type semiconductor.[7] The lattice structure of CaB₆ is simple cubic space group *Pm3m* with each corner occupied by boron octahedral cages and body center occupied by the Ca atom. The lattice of CaB₆ reveals a framework like morphology with a tunnel like structure at the center which could render potential pathways for ion intercalation in energy storage

applications. In general, the alkaline earth hexaborides are used as neutron radiation absorbers, protective coating in high temperatures and wear resistant applications and as n-type thermoelectric materials [8–10]. Recently Yin et al. investigated CaB₆ as an active anode material for aqueous primary battery and reported a specific capacity of 2400 mAh/g in 30% KOH solution [11]. Because of its light weight, chemical inertness, relatively good conductivity, and tunnel like lattice structure, CaB₆ could be an interesting material for energy storage applications. In this communication, the energy storage behavior of CaB₆ particulates as electrode material for electrochemical capacitors is reported.

2. Experimental

A slurry containing calcium hexaboride particulates (99.5% purity, –325 mesh,), 2–5 wt% acetylene carbon black, 2 wt% polyvinylidene fluoride (PVDF) dissolved in N,N Dimethylformamide was coated onto a graphite substrate using doctor-blade technique to achieve different coating thicknesses by applying multiple layers. The starting materials were obtained from Alfa Aesar. The coating was dried at 250 °C for 2 h under vacuum. Cyclic voltammetry (CV) experiments were carried out at different scan rates on the CaB₆ samples to optimize the additives and thickness of the coating using a three-electrode configuration with Pt-spiral as a counter electrode and AgCl coated Ag wire as a reference electrode. The electrolyte was 1 m LiPF₆ dissolved in 50/50 ethyl carbonate and dimethyl carbonate (from Aldrich). An in-house made sealable flat cell that is capable of exposing only 1 cm² area of the sample was used in all the electrochemical experiments. The electrochemical cell was assembled inside a dry glove box and

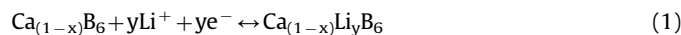
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purged with argon. The experiments were carried out outside the glove box after sealing the cell air-tight. Based on the CV results, a single layer coating containing 12 mg/cm² of active material and 2 wt% of carbon black was observed to yield the highest capacitance. Therefore, further experiments such as galvanostatic charge-discharge at different current densities, and electrochemical impedance spectroscopy (EIS) were carried on the single layer coated CaB₆ samples. Galvanostatic charge-discharge experiments were carried out, using a three-electrode configuration similar to that of CV experiments, at different current densities in the range of 1–30 mA/cm². EIS was carried out at the open circuit potential of the samples by imposing an ac potential of 10 mV and scanning the frequency from 100 kHz to 0.01 Hz. Mott-Schottky analysis was carried out at 100 Hz by 100 mV-step-wise scanning of the potential from anodic to cathodic direction. The structure of the CaB₆ coating was characterized using XRD.

3. Results and discussion

The surface morphology of the CaB₆ electrode, and its XRD pattern are given in the Fig. S1 (Supporting information). Since the electrodes were prepared by the slurry-cast method, the actual surface area was larger than the exposed geometric area. The estimated specific surface area of the electrode was about 1240 cm²/g. Fig. 1(a) shows the initial cyclic voltammograms of CaB₆ in 1 m LiPF₆ non-aqueous electrolyte at different scan rates. The variation in the current density during potential scanning and current peak during the anodic scan indicated contribution from possible Faradaic reactions in addition to the interfacial double layer capacitance. Specifically, the increase in the current density at potentials more negative than –2.5 V could be attributed to the adsorption of lithium on the CaB₆. Under-potential deposition of lithium on to noble metals has been reported at about –2.5 V Vs Ag (+0.5 V Li/Li⁺) [12]. The low work function of CaB₆, and presence of fluoride species could promote either under potential deposition (UPD) or adsorption of lithium onto CaB₆ at preferred sites [13]. The mechanism of UPD of lithium is not the focus of this study. The sharp increase in the cathodic current below –2.5 V and an anodic peak during reverse scan suggested the pseudo capacitance due to redox reactions of lithium from the electrolyte. The lithium adsorption, and surface diffusion followed by the intercalation into the CaB₆ could be given by the reaction:



The above reaction was observed to be facilitated by the Ca

vacancies present in the as-prepared electrode. Increase in the scan rate did not increase the current density, which again could be attributed to the diffusion controlled Faradaic reactions that determined the capacitance of the electrode. Fig. 1(b) shows the cyclic voltammograms at 100th cycle. The maximum current densities decreased significantly after 100 cycles. The capacitance calculated from the CV at 100 mV/s scan rate for the first and hundredth cycle were 34 and 25 F/g, respectively indicating about 25% loss.

Fig. 2(a) and (b) illustrates the galvanostatic charge-discharge behavior of the CaB₆ at 5 and 30 mA/cm² current densities. Two different slopes were observed for both the charge and discharge conditions. The abrupt changes in the potentials were due to the charge-discharge of the interfacial double layer and not due to the IR drop. The abrupt change in potential was followed by a drooping potential with shallower slope which indicated the occurrence of redox reactions. The pseudo-capacitance discharge occurred at more positive potentials (around 0.8 V) at the 5 mA/cm² condition than that of 30 mA/cm² condition (around –2.3 V). The potential windows were different for the different current densities. At 30 mA/cm², the charging occurred at potentials more negative to the Li/Li⁺ redox potential suggesting incorporation of lithium in the electrode. Therefore, the discharge potential more positive to –2.3 V could be attributed to the oxidation of lithium. This observation indicates that CaB₆ could intercalate lithium and be used as an anode for Li-ion battery. However, when charged at 5 mA/cm², the potential was below the UPD potential of lithium and the discharge plateau at about 0.8 V could be associated with oxidation of CaB₆ due to the trace amount of water possibly incorporated in the electrolyte. The specific capacitance values were 35.7 and 18.2 F/g for the 5 and 30 mA/cm² charge-discharge conditions, respectively. The average discharge efficiencies were about 88% and 62% for the 5 and 30 mA/cm² current densities, respectively.

Fig. 3(a) and (b) shows the EIS and Mott-Schottky results of the sample charge-discharge tested at 30 mA/cm², respectively. The EIS data of the un-tested (as-prepared) sample and the equivalent circuit analyses are given in Figs. S2 and S3 (Supporting information). The as-prepared sample did not show a diffusion controlled Warburg component. Whereas, the Warburg resistance appeared for the sample charge-discharge tested at 30 mA/cm² Table S1.

(Supporting information) summarizes the magnitude of the equivalent circuit components. The slope of the Bode plot (Fig. 3 (a)) is –0.51 which also indicated presence of the Warburg resistance in series with the charge transfer resistance of the sample. Based on the Warburg coefficient, the diffusion coefficient was

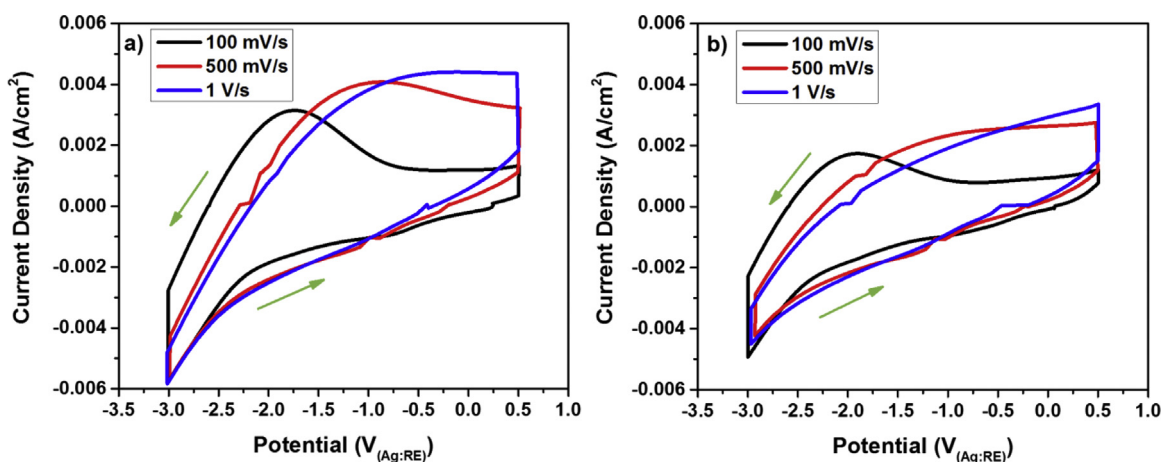


Fig. 1. Cyclic voltammograms of CaB₆ coatings tested at different scan rates in 1:1 PC:EC electrolyte containing 1 m LiPF₆. (a) CV of 1st cycle; and (b) CV of 100th cycle. The capacitance loss after 100 cycles was about 25% as compared to the initial capacitance.

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