



Short communication

Enhanced electrochemical properties of nanostructured bismuth-based composites for rechargeable lithium batteries

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ABSTRACT

Nanostructured Bi/C and Bi/Al₂O₃/C composites, prepared by high-energy mechanical milling (HEMM), are investigated as anode materials for Li-ion rechargeable batteries. X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) reveal that the Bi/C nanocomposite is composed of nano-sized Bi and amorphous C, while the Bi/Al₂O₃/C nanocomposite (obtained by the mechanochemical reduction of Bi₂O₃ and Al) is composed of nano-sized Bi, amorphous Al₂O₃, and amorphous C. The electrochemical reaction mechanism of the Bi/C nanocomposite electrode is identified by *ex situ* XRD analyses combined with a differential capacity plot. Electrochemical tests show that the Bi/C and Bi/Al₂O₃/C nanocomposites exhibit enhanced electrochemical performances compared with that of the pure Bi electrode.

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1. Introduction

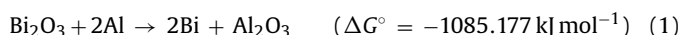
Over the past decade, there has been intensive research focusing on increasing the specific energy and energy density of rechargeable Li-ion batteries in order to satisfy the growing need for longer-lasting electronic mobile devices. At present, graphite (LiC₆: 372 mAh g⁻¹, ca. 840 mAh cm⁻³) is used as an anode material for lithium secondary batteries. Nevertheless, higher-capacity alternatives are being actively pursued, especially for the anode materials. Among the many possible alternatives, many studies have been devoted to group IV (Si, Ge, Sn) [1–8] and group V (P, As, Sb, Bi) [9–16] elements. This is due to their ability to react reversibly with large amounts of Li per formula unit (to form lithium alloys). Although alloy-based systems have a higher energy density, they suffer from poor cycling behaviour, since a large volume change occurs during charge/discharge.

Many research groups have suggested nano-sized materials as alternatives to alleviate the volume-change problem [17–19]. Although nano-sized particles show a better cyclic performance, they have a few demerits, such as aggregation during cycling (caused by a high surface reactivity) and poor coulombic effi-

ciency during the first cycle (due to the remaining salts or oxides that formed during their syntheses). Consequently, nanocomposite materials containing carbon can be considered to be candidates as the anode material of lithium secondary batteries [11–13,20–23].

Lithium can react with Bi, which has a gravimetric capacity of 386 mAh g⁻¹ (Li₃Bi) and a high volumetric capacity of ca. 3800 mAh cm⁻³. The high volumetric capacity of Bi means that it is a promising anode material for lithium secondary batteries. This is because volumetric capacity is more important than gravimetric capacity for the practical application of battery systems in electronic mobile devices. Although there have been several studies focusing on the reactions of thin-layer or nano-sized Bi, poor electrochemical performances have been reported [15,16].

In this study, a Bi/C nanocomposite is simply prepared by a straightforward high-energy mechanical milling (HEMM) technique to enhance the electrochemical behaviour of Bi. The phase changes of the Bi/C nanocomposite are investigated during Li insertion/extraction. In addition, a Bi/Al₂O₃/C nanocomposite is prepared via the following reaction:



where ΔG° is the standard free energy.

Based on the concept of an active–inactive matrix and the mechanical strengthening of the active material during cycling [24,25], this reaction is proposed as a method for enhancing the

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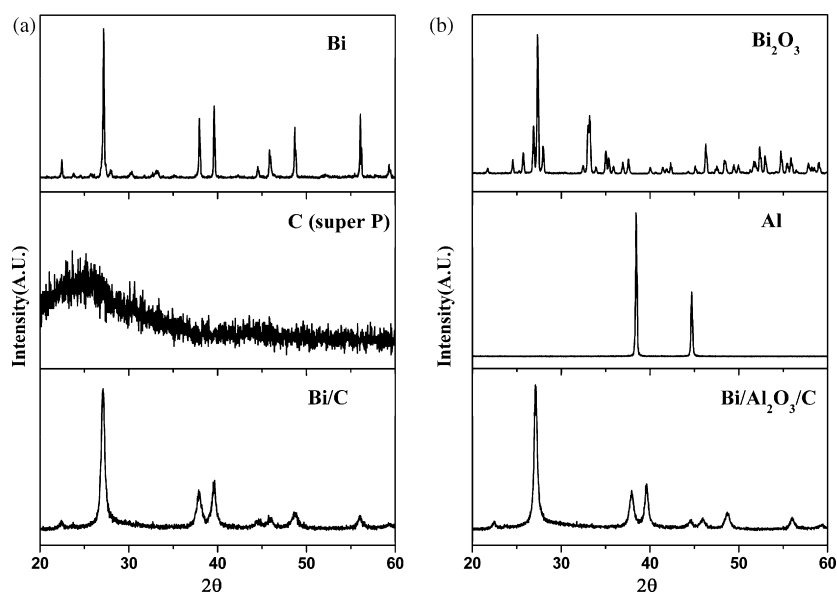


Fig. 1. X-ray diffraction patterns of: (a) Bi, amorphous C (Super P), and Bi/C nanocomposite and (b) Bi₂O₃, Al, and Bi/Al₂O₃/C nanocomposite.

electrochemical performances of this alternative anode material for Li rechargeable batteries.

2. Experimental

The Bi/C nanocomposite was prepared as follows. Bismuth (Aldrich, 99.995%, –100 mesh), nano-carbon (Timcal, Super P, –100 nm), and stainless-steel balls (diameter: 3/8 and 3/16 in.) were placed in a hardened steel vial of capacity 80 cm³, with a ball-to-powder ratio of 20:1. The HEMM process (Spex-8000) was conducted under an Ar atmosphere for 12 h. Preliminary studies showed that the optimum amounts of Bi and C were 80 and 20 wt.%. The Bi/Al₂O₃/C nanocomposite was prepared using the same method as above, but with Bi₂O₃ (Aldrich, 99.9%, 10 μm), Al (Kojundo, 99.9%, 20 μm) and nano-carbon (Super P). Preliminary studies also showed that the optimum amounts of Bi₂O₃+Al and C were 80 and 20 wt.%. Also, the amount of amorphous Al₂O₃ was estimated to be ca. 15.7 wt.%.

The Bi/C and Bi/Al₂O₃/C nanocomposite samples were characterized by means of X-ray diffraction (XRD, Rigaku, D-MAX2500-PC), scanning electron microscopy (SEM, JEOL JSM-6360), and high-resolution transmission electron microscopy (HRTEM, JEOL 3000F operating at 300 kV). The *ex situ* XRD method was used to observe the phase changes in the active material during cycling. The electrodes were detached from the cell and coated with polyimide tape (Kapton) as a protective film. For TEM analysis, a dilute suspension of the sample was dropped on to a carbon-coated TEM grid and then allowed to dry.

For electrochemical evaluation of the Bi and its nanocomposites, the test electrodes consisted of the active powder material (70 wt.%), carbon black (Denka black, 15 wt.%) as a conductor, and polyvinylidene fluoride (PVDF) dissolved in *N*-methyl pyrrolidone (NMP) as a binder (15 wt.%). Each component was well mixed to form a slurry that was coated on a copper foil substrate followed by pressing and drying at 120 °C for 4 h under vacuum. Laboratory-made, coin-type, electrochemical cells were assembled in an Ar-filled glove-box using Celgard 2400 as the separator, Li foil

as the counter and reference electrodes, and 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 (v/v), Samsung) as the electrolyte. All of the cells were tested galvanostatically between 0.0 and 2.0 V (vs. Li/Li⁺) at a current density of 100 mA g⁻¹ using a Maccor automated tester. The gravimetric capacity was calculated with respect to all active elements (such as Bi and C), while the volumetric capacity was obtained from the gravimetric capacity by multiplying the density of Bi by the weight percent of Bi (80%). The actual volumetric capacity would be higher than the obtained value. Lithium was inserted into the electrode during charging and was extracted from the working electrode during discharging.

3. Results and discussion

The XRD patterns of the Bi/C and Bi/Al₂O₃/C nanocomposites are given in Fig. 1(a) and (b), respectively. All of the peaks of the Bi/C nanocomposite correspond to Bi, and no other crystalline phases are detected. In the XRD pattern of the Bi/Al₂O₃/C nanocomposite prepared by reaction (1) all of the peaks correspond to Bi; other phases, such as Al₂O₃, are not apparent.

Scanning electron micrographs of the original Bi and milled Bi powders are presented in Fig. 2(a) and (b), respectively. The particle sizes of the milled Bi powder are reduced to less than 5 μm. The TEM bright-field and HRTEM images with selected-area diffraction (SAD) patterns and lattice spacing of the Bi/C nanocomposite are given in Fig. 2(c) and (d), respectively. These show that the Bi/C nanocomposite material consists of agglomerated nano-sized crystalline Bi and amorphous C. The morphologies of the nano-crystalline Bi, amorphous Al₂O₃, and amorphous C in the Bi/Al₂O₃/C nanocomposite were also identified by means of TEM bright-field (Fig. 2(e)) and HRTEM images (Fig. 2(f)) with the Fourier transformed (FT) pattern for the selected area. The average crystallite size of Bi (estimated using Scherrer's equation) is ca. 100 nm before milling and is reduced to approximately 10 nm in the milled Bi/C and Bi/Al₂O₃/C nanocomposites, as shown in Fig. 2(d) and (f), respectively.

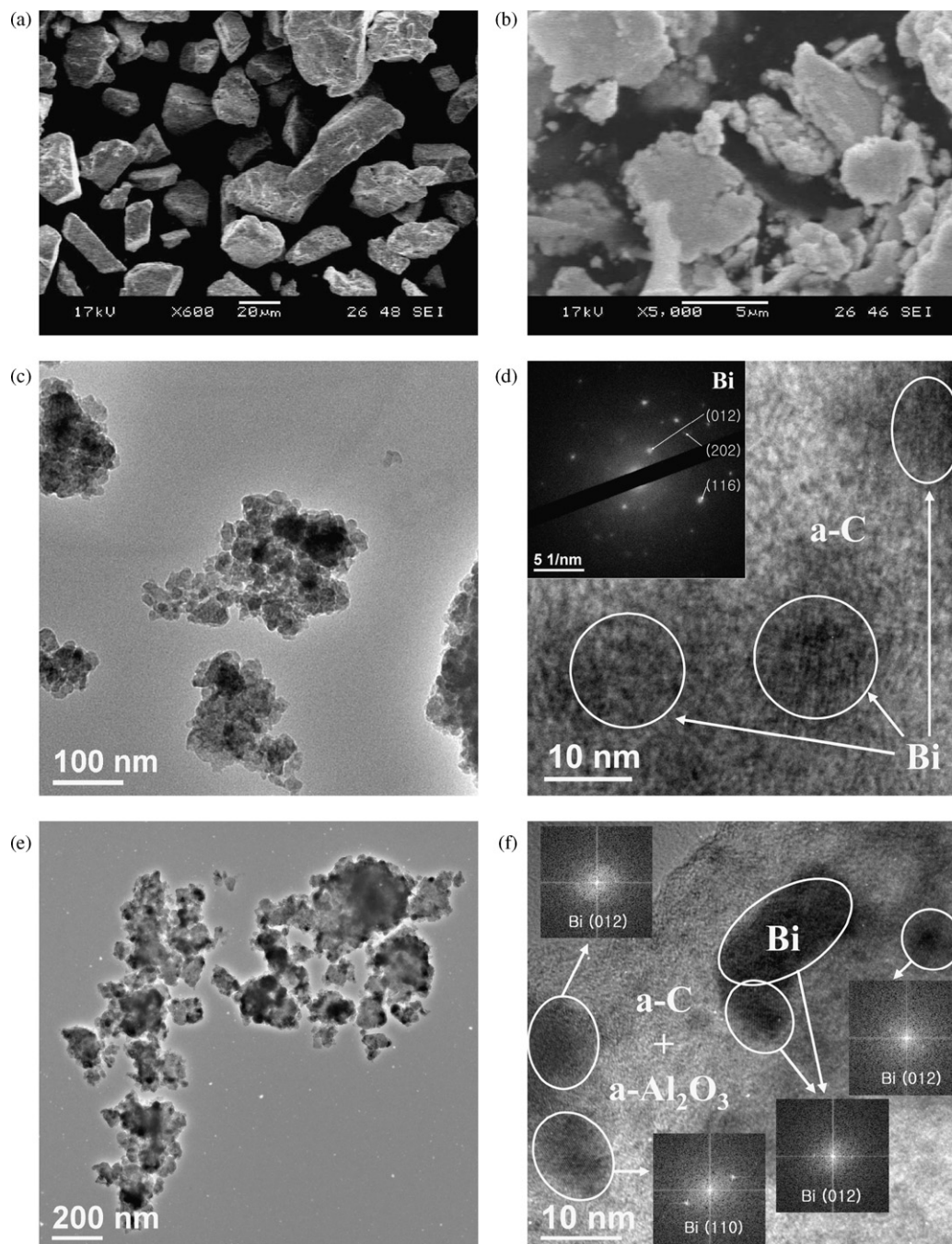


Fig. 2. (a) SEM image of original Bi, (b) SEM image of milled Bi, (c) TEM image of Bi/C nanocomposite, (d) HRTEM image of Bi/C nanocomposite with selected-area diffraction patterns and lattice spacing of Bi, (e) TEM image of Bi/Al₂O₃/C nanocomposite, and (f) HRTEM image of Bi/Al₂O₃/C nanocomposite with FT patterns and lattice spacing of Bi.

The voltage profiles of the Bi, milled Bi, Bi/C nanocomposite, and Bi/Al₂O₃/C nanocomposite are presented in Fig. 3(a–d), respectively. The first charge and discharge capacities, with a coulombic efficiency for the first cycle of each electrode, are

presented in Table 1. It can be seen that the pure Bi electrode shows a very poor reversibility. Although the milled Bi electrode displays enhanced reversibility due to the reduced particle size, the capacity fades rapidly after a few cycles. The dras-

Table 1
Comparisons of first charge and discharge capacity, first cycle coulombic efficiency and cycle retention of various electrodes.

Electrode	First charge capacity (mAh g ⁻¹)	First discharge capacity (mAh g ⁻¹)	First cycle coulombic efficiency (%)	Cycle retention (Xth/1st discharge) (%)
Bi	440	196	45	88 (X=10)
Milled Bi	505	432	86	52 (X=10)
Bi/C	663	471	71	91 (X=10), 61 (X=100)
Bi/Al ₂ O ₃ /C	598	423	71	95 (X=10), 74 (X=100)

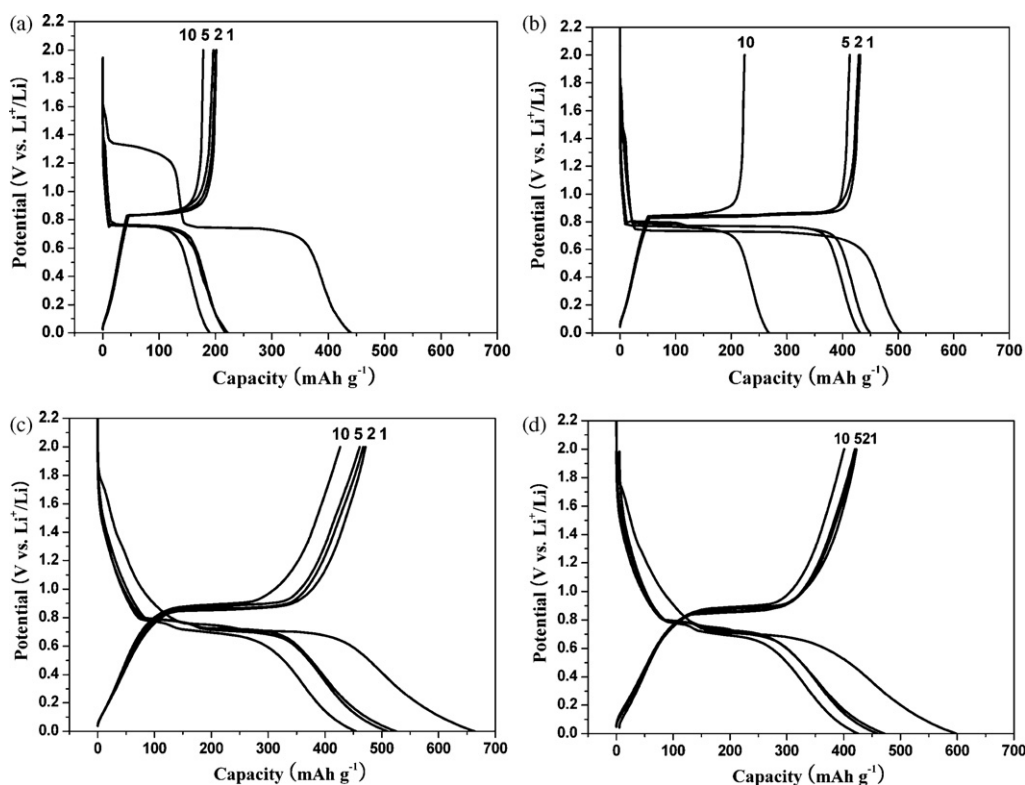
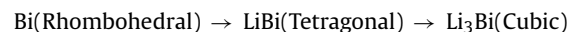


Fig. 3. Electrochemical behaviour of: (a) Bi, (b) milled Bi, (c) Bi/C nanocomposite, and (d) Bi/Al₂O₃/C nanocomposite.

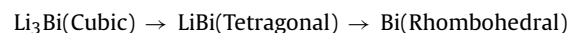
tic capacity decreases of the Bi and milled Bi electrodes are caused by the large volume change associated with the pulverization of the active material, and its electrical isolation from the current-collector. The coulombic efficiency of the first cycle for the Bi/C nanocomposite electrode is about 71%, which confirms its enhanced electrochemical reversibility. Given that the irreversible capacity of the milled C in the Bi/C nanocomposite is approximately 100 mAh g⁻¹, both the preparation of the nano-sized active Bi particles and the prevention of their aggregation by incorporating carbon (using the HEMM technique) contribute to the enhanced cycleability of the milled Bi electrode compared with that of the pure Bi. In Fig. 3(d), the Bi/Al₂O₃/C nanocomposite electrode shows the better cycle retention of approximately 95%, with a high capacity about 400 mAh g⁻¹ (ca. 3100 mAh cm⁻³) after 10 cycles, although the first charge capacity is slightly reduced by the presence of the inactive amorphous Al₂O₃ phase.

The differential capacity plot (Fig. 4(a)) of the first cycle of the Bi/C nanocomposite electrode shows two peaks during charging, along with one very large peak during discharging. *Ex situ* XRD analyses were performed at selected potentials, as indicated in the differential capacity plot, and the results are presented in Fig. 4(b). When the potential is lowered from 2 to 0.73 V (corresponding to 1 mol of Li per mole of Bi), a LiBi phase appears and some of it is transformed into a Li₃Bi phase, as shown in Fig. 4(b)-ii. When the electrode is in a fully charged state (0.0 V, Fig. 4(b)-iii), the XRD pattern shows the presence of the Li₃Bi phase only. During discharging, the Li₃Bi phase disappears, and the LiBi phase starts to reappear (Fig. 4(b)-iv). In the fully discharged state (2 V, Fig. 4(b)-v), only the Bi phase peaks can be observed. Based on the above *ex situ* XRD results, the reactions involved during the first charge and discharge are as follows:

- During charge:



- During discharge:



Similar results were obtained by Xianming et al. [15] using a thin-layer Bi electrode.

Comparisons of the cycle performance were made for the Bi, milled Bi, Bi/C, and Bi/Al₂O₃/C nanocomposite electrodes, when cycled within the voltage range of 0.0–2.0 V. As shown in Fig. 5, the cycle performances of the Bi and milled Bi electrodes are very poor. The capacity retention of the Bi/C nanocomposite is much enhanced compared with those of the Bi and milled Bi electrodes, but its capacity decreases gradually with each cycle. This is caused by mechanical cracking and crumbling, which arise due to the large volume change caused by the formation of the Li₃Bi phase. The Bi/Al₂O₃/C nanocomposite electrode gives a relatively stable capacity of approximately 310 mAh g⁻¹ (ca. 2400 mAh cm⁻³) over 100 cycles, and the capacity retention is about 74% of the discharge capacity of the first cycle. This is better than the capacity retention (ca. 61%) of the Bi/C nanocomposite. The good electrochemical properties of the Bi/Al₂O₃/C nanocomposite electrode are due to it having uniformly distributed nano-sized Bi crystallites, the presence of the inactive amorphous Al₂O₃ which can accommodate the strain generated during the cycling, and the buffering effect of the amorphous carbon matrix.

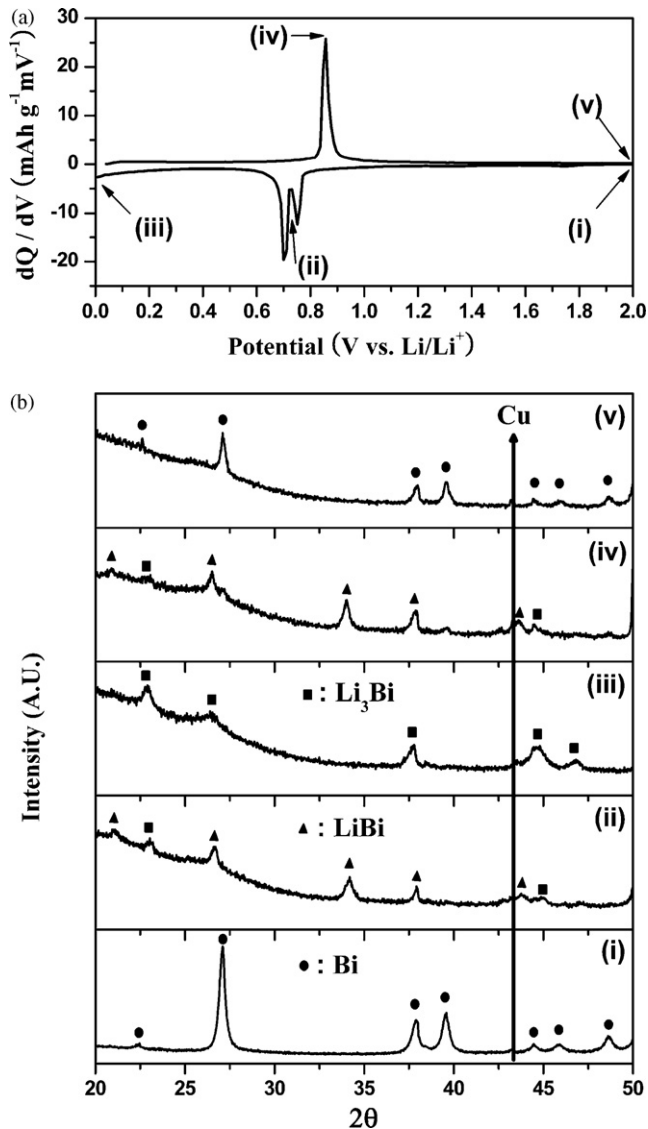


Fig. 4. (a) Differential capacity plot and (b) X-ray diffraction patterns (small Greek numbers correspond to potential indicated in (a)) of Bi/C nanocomposite for first cycle.

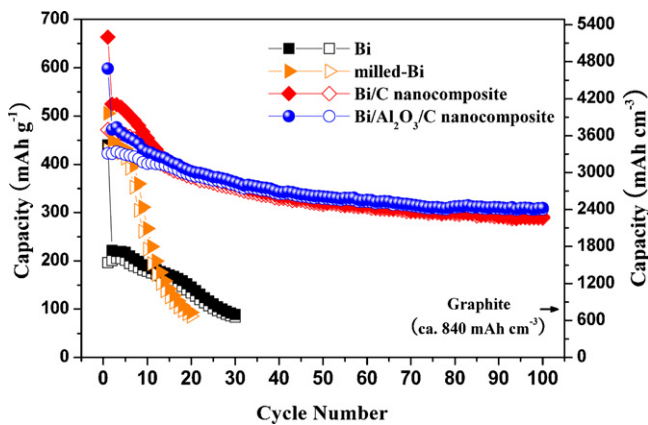


Fig. 5. Comparison of the cycle performances of Bi, milled Bi, Bi/C, and Bi/Al₂O₃/C nanocomposites.

4. Conclusions

Nanostructured Bi-based composites were prepared by HEMM in an attempt to enhance the electrochemical properties of Bi. When used as an anode material for Li rechargeable batteries, the Bi/C nanocomposite electrode shows enhanced electrochemical charge–discharge behaviour, with a high volumetric capacity. Moreover, the Bi/Al₂O₃/C nanocomposite electrode displays even better cycle behaviour than the Bi/C nanocomposite electrode. The large volumetric capacities and good cycleabilities of the Bi-based composite electrodes make them promising new anode materials for Li-ion batteries.

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