

Excess volume in nanocrystalline lithium-carbon system

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A method that combines model calculations with X-ray diffraction analyses on prepared nanocrystalline samples has been developed to determine the excess volume and its dependence on grain size in nanocrystalline anode materials. In the model calculations, the geometry of grains in nanocrystalline systems is treated as a spherical shape for simplicity. It has been determined that the excess volume depends on grain size and atomic density at grain boundaries. The nanocrystalline Li₂C₂ alloy was taken as an example of the nanostructured anodes and its grain boundary expansion was generated by the excess volume at different grain size levels.

1. Introduction: There is increasing interest in nanostructured materials as candidates for high-performance Li ion battery (LIB) anodes [1]. It was reported that nanostructuring of LIB anode materials improved significantly the electrochemical properties with respect to the conventional coarse grained counterparts, such as high reversible power capacity, fast charging, long cycle life and high safety in a variety of material systems [2, 3]. The enhancement in performance of nanostructured anode materials is mainly attributed to the large volume fraction of the interface (grain boundaries and phase boundaries), which provide a faster transport path for the Li ions upon loading [4]. Moreover, the interface with a high-volume fraction in nanocrystalline materials can provide some excess volume that allows additional storage of Li ions and generates better accommodation strain because of the volume change in the process of charging and discharging [5]. However, the characterisation and the influencing factors of the excess volume in nanocrystalline anode materials have not yet been well understood. It is very important to quantify the excess volume of nanocrystalline anode materials. Some approaches such as high-resolution transmission electron microscopy [6], positron annihilation [7] and dilatometry [8] have been proposed to estimate the value of excess volume at the grain boundaries. These methods provided insights towards the characterisations of excess volume in nanocrystalline materials through calculations of stress and investigations on the interface migration and grain growth; however, consistent results for quantification of the excess volume and its dependence have not been attained so far.

In this Letter, we present an alternative method that combines the appropriate model calculations with X-ray diffraction (XRD) measurements on the prepared nanocrystalline samples to determine the excess volume at grain boundaries, as well as its dependence. As one of the most promising anode systems for LIBs [1], the Li-C system is taken as an example in this study. The quantification of the excess volume and the discovery of its influencing factors may facilitate the design of the nanostructured anode materials for high-performance LIBs.

2. Method: The nanocrystalline materials can be described as composed of two components: the crystalline component constructed by atoms in the lattice of crystallites (grain interiors) and the interfacial component constructed by the atoms at the interface between crystallites (grain boundaries) [9]. At the grain boundaries, the number of the nearest neighbours of a centred atom is reduced as compared with that in the perfect crystal structure, which leads to a decrease in the atomic density at the grain boundaries, ρ_b [10]. In the nanocrystalline materials, ρ_b is

lower than the atomic density in the perfect crystal structure, ρ_0 , by up to ~30% when the grain size is sufficiently small [11]. The atomic densities at the grain boundaries and in the grain interiors can be defined as $\rho_b = 1/V_b$ and $\rho_0 = 1/V_0$ [12], respectively, where V_b and V_0 are the respective atomic volumes at the grain boundaries and in the grain interiors. Accordingly, the relationship $\rho_b/\rho_0 = V_0/V_b = 1/(1 + \Delta V)$ is obtained based on the definition of the excess volume ΔV at the grain boundaries in the nanocrystalline materials, that is, $\Delta V = V_b/V_0 - 1$ [13]. The parameters such as ρ_b , V_b and ΔV , which are related to the grain boundary characteristics, are all dependent on the grain size. With decreasing the grain size d , ρ_b decreases whereas V_b and ΔV increase. To describe the grain size dependence of the atomic density, a relationship $\rho_b/\rho_0 = A + Bd^C$ is assumed for the nanocrystalline materials, where A , B and C are the undetermined constants for a given crystal structure. With this relationship, the excess volume and the atomic volume at the grain boundaries are obtained as a function of the grain size, that is, $\Delta V = -1 + 1/(A + Bd^C)$, $V_b = V_0/(A + Bd^C)$. The constants A , B and C can be fitted given that three pairs of V_b (or ΔV) and d are known. However, the direct measurements of V_b and ΔV in the nanocrystalline materials are usually very hard using present technologies. Here, we present an approach to obtain the corresponding values of V_b (or ΔV) and d on the basis of XRD measurements for the prepared nanocrystalline samples.

On the one hand, the molar volume V^{mc} of a nanocrystalline material can be expressed as $V^{mc} = N[(1 - x_b)V_0 + x_bV_b]$, where N is the number of atoms and x_b is the atomic fraction at the grain boundaries. The parameter $x_b = f_b/(1 + \Delta V - \Delta V/f_b)$ is obtained assuming that the grains in the nanocrystalline material are of spherical shape with a diameter of d and a grain boundary thickness of h and the volume fraction of grain boundaries can be calculated as $f_b = 1 - (d - h)^3/d^3$. On the other hand, the molar volume V^{mc} and grain size of the prepared nanocrystalline materials can be obtained by the Rietveld refinement [14] based on the XRD patterns. By combining the model calculations and the experimental measurements, as described above, one can obtain the excess volume at grain boundaries at a given grain size in the nanocrystalline materials. Given three (or more) pairs of values of the excess volumes and grain sizes for the prepared nanocrystalline samples, the constants A , B and C can be obtained. Thus, the relationship between the excess volume and the grain size is determined quantitatively.

3. Experiments: Owing to the very high activity of the Li-C system towards oxygen and water [15], all the processing steps were

performed in a home built *in situ* fabrication system with a fully closed circumstance [16], where the environmental oxygen and water concentrations were controlled below 5 ppm. The equipment system combined powder treatment and spark plasma sintering in the closed system filled with highly purified argon gas. The coarse grained polycrystalline Li_2C_2 ingot was prepared by melting pure lithium and graphite. Then the ingot was milled and the amorphous powder was obtained. To prepare the nanocrystalline Li_2C_2 bulk materials with different grain size levels, the amorphous powder was sintered using a constant pressure of 300 MPa and different final temperatures as 523, 623 and 673 K. The sintering temperatures were designed according to the crystallisation behaviour of the amorphous powder, measured by differential scanning calorimetry. The XRD patterns of the samples were detected by the SHIMADZU-7000X diffractometer with the monochromatic $\text{Cu K}\alpha$ radiation. The Rietveld refinement was performed for the samples based on their XRD data, from which both the crystal structure (crystal lattice parameters, atomic positions and occupancies) and microstructure parameters (mean grain size) can be obtained.

Fig. 1 shows the XRD analyses on the phase constitution and crystal structure of the Li_2C_2 samples prepared at different sintering temperatures. It can be seen that all the samples have the single phase of Li_2C_2 and no impurity phase is observed. The XRD data of curve (a) in Fig. 1 shows that in the coarse grained ingot system, the stable phase at room temperature is $\alpha\text{-Li}_2\text{C}_2$ with an orthorhombic structure, which is in agreement with the previous results in the literature [15, 17]. By ball milling the amorphous powder is obtained from the ingot, as indicated by curve (b) in Fig. 1. The XRD patterns of the Li_2C_2 bulk samples sintered at 523, 623 and 673 K are shown by curves (c), (d) and (e) in Fig. 1, respectively. It is found that the sample sintered from the amorphous powder at the relatively lower temperature of 523 K consists of $\alpha\text{-Li}_2\text{C}_2$ as a dominant phase and $\beta\text{-Li}_2\text{C}_2$ as a minor phase. In the conventional coarse grained Li-C alloy system, the $\beta\text{-Li}_2\text{C}_2$ phase with a face centred cubic structure can only be stable at temperatures higher than ~ 700 K [15]. Therefore a different phase stability occurs in the sample prepared at 523 K. The other samples sintered at higher temperatures contain only the single $\alpha\text{-Li}_2\text{C}_2$ phase.

The lattice parameters were obtained by the Rietveld refinement and the mean grain sizes of the three Li_2C_2 bulk samples were calculated by the Scherer formula based on the XRD data. The results showed that the mean grain sizes were about 10, 17 and 21 nm in the bulk samples sintered at temperatures of 523, 623 and 673 K, respectively. Owing to the ultrafine nanocrystalline structure in

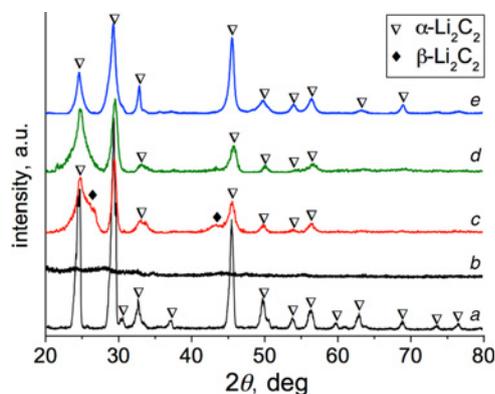


Figure 1 XRD patterns and indexing of the Li_2C_2 samples at different preparation stages
a As-cast ingot
b Ball-milled powder
c–e Bulk samples sintered at temperatures of 523, 623 and 673 K, respectively

Table 1 Mean grain size, molar volume and excess volume at different grain boundary thickness of the nanocrystalline Li_2C_2 alloy

Mean grain size, d , nm	Molar volume, V_m^{nc} , $\text{\AA}^3/\text{atom}$	Excess volume, ΔV	
		$h = 6r_0$	$h = 6r_b$
10	12.518	0.221	0.207
17	12.236	0.168	0.160
21	12.165	0.147	0.139

the bulk sample sintered at 523 K, the anomalous stability of the Li_2C_2 phase results from the nanoscale effect on the energy state of the system. As can be described quantitatively by the nanothermodynamic model [18–20], when the grain size is reduced to below a critical value, the Gibbs free-energy of the nanocrystalline system can be lower than that of the coarse-grained polycrystalline counterpart. As a consequence, the phase that is metastable at room temperature in the coarse grained system can be stabilised in an ultrafine nanocrystalline structure. Moreover, as compared with the lattice parameters of the coarse-grained polycrystalline Li_2C_2 as $a = 3.652$ \AA , $b = 4.831$ \AA and $c = 5.434$ \AA [15], the lattice parameters increase by 1.0–2.0% when the mean grain size is reduced to ~ 10 nm in the nanocrystalline sample.

4. Grain-size-dependent excess volume: In the following, we combine the refined crystal structure parameters of the nanocrystalline Li_2C_2 samples and proper model calculations to determine the grain-size-dependent excess volume for the nanocrystalline Li-C system. On the one hand, the values of molar volume (see Table 1) for each nanocrystalline sample were obtained according to their lattice parameters. It is found that as

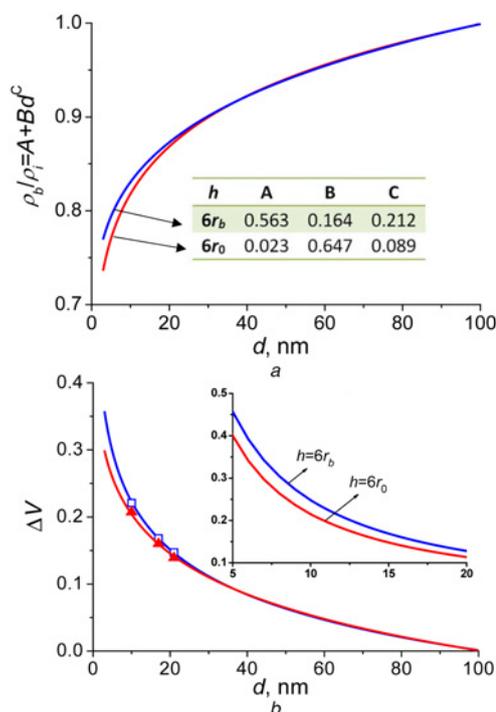


Figure 2 Results of the relationship $\rho_b/\rho_0 = A + Bd^c$ and the excess volume against grain size
a Grain size dependence of the relative atomic density (ρ_b/ρ_0)
b Relationship between the excess volume and the grain size
Inset: The local enlargement. The symbols \square and \blacktriangle represent the experimentally determined values of the excess volume at different grain boundary thickness

compared with the coarse grained polycrystalline phase, the molar volume of the nanocrystalline Li_2C_2 phase increases by $\sim 4.5\%$ when the mean grain size decreases to ~ 10 nm. Accordingly the excess volumes of different nanocrystalline samples with various mean grain sizes are obtained. On the other hand, based on the theoretically obtained expression of molar volume for nanocrystalline materials (which is a function of excess volume and grain size with three undetermined constants), the fitting process is carried out using the experimentally obtained molar volumes. As a result, the grain-size-dependent excess volume is determined for the nanocrystalline Li-C system; the fitted constants are shown in the inset in Fig. 2a.

It should be noted that the grain boundary thickness, h , in the nanocrystalline material varies generally in an order of $0.5\text{--}1$ nm [21], which is approximately equivalent to $2\text{--}4$ atomic layers ($h = 6r_0$ is assumed for the nanocrystalline Li-C system in the present model calculation, r_0 represents the atomic radius in the perfect crystal). In previous studies, the grain boundary thickness was considered to be independent on the grain size and the phase stability [22]. However, for the nanocrystalline materials with ultrafine grain size, it has been found that the lattice distortion in the vicinity of grain boundaries is large enough so that the grain boundary thickness does not remain constant but depends on the grain size [23]. Caro *et al.* [24] pointed out that neglecting the relation between grain boundary thickness and grain size may cause ambiguous explanations for the nanomaterials [25]. In our method, a formula $h = nr_b = nr_0(\Delta V + 1)^{1/3}$ is used to represent the change of the grain boundary thickness with the grain size on the nanoscale, where n is the number of atomic layers at the grain boundaries, r_b is the atomic radius at the grain boundaries and $\Delta V = r_b^3/r_0^3 - 1$. Taking into account the effect of the grain boundary thickness and its dependence on the grain size, we obtained the excess volumes of each nanocrystalline sample, as listed in Table 1.

From the experimentally determined three pairs of values for the excess volumes at different grain sizes, the constants A , B and C in the formula $\rho_b/\rho_0 = A + Bd^C$ are known and the grain-size-dependent function of the excess volume can be obtained. Figs. 2a and b show the results of the relationship $\rho_b/\rho_0 = A + Bd^C$ and the excess volume as a function of the grain size, respectively. The atomic density at the grain boundaries decreases obviously with the decrease of grain size and the decrease may reach $\sim 25\%$ when the grain size is reduced to a few nanometres scale, correspondingly, the excess volume attains a value of ~ 0.3 .

The grain boundary expansion, e_{GB} , defined as the change of volume V^{nc} with the grain boundary area S^{nc} at a constant temperature T for a nanocrystalline phase, that is, $e_{\text{GB}} = (dV^{\text{nc}}/dS^{\text{nc}})_T$ [8], can be calculated as a function of grain size on the basis of grain-size-dependent excess volume and atomic fraction at grain boundaries. As shown in Fig. 3, the value of e_{GB} in the nanocrystalline Li-C system increases from 0.75×10^{-10} to 1.8×10^{-10} m as

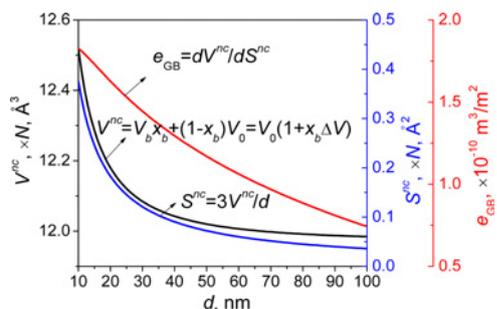


Figure 3 Grain boundary expansion e_{GB} against grain size d in the nanocrystalline Li_2C_2 phase

Note that the grain boundary area S^{nc} is deduced from the volume V^{nc} with the assumption of spherical grains in the nanocrystalline material

the grain size decreases from 100 to 10 nm. The grain boundary expansion is in an order of magnitude as 10^{-10} m, which is one order smaller than the grain boundary thickness. This is consistent with the previous measurements on the excess volume in various nanocrystalline materials, such as the values of about 1.7×10^{-10} m for the nanocrystalline Pd with a mean grain size of 18 nm [26] and about 1.6×10^{-10} m for the nanocrystalline Ni with a mean grain size of 29 nm [27]. Much smaller excess volumes have been measured in the submicron or micron grained polycrystalline materials with values in a range of 0.1×10^{-10} – 0.6×10^{-10} m [8, 28].

5. Conclusion: In summary, by combing the model calculation with the Rietveld analysis based on the XRD data of the prepared nanocrystalline samples, a method has been developed to quantify the grain size dependence of the excess volume in the nanocrystalline anode material system. With the present approach, the relationship between the excess volume and the grain size, the atomic density at grain boundaries and the atomic fraction of grain boundaries in the nanocrystalline anode materials can be determined quantitatively. The application of the present method to nanocrystalline Li_2C_2 indicates the feasibility of obtaining the excess volume in nanocrystalline anode materials, which facilitates the development of nanostructured anodes for high performance lithium ion batteries.

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