High-capacity carbons prepared from acrylonitrile-butadiene-styrene terpolymer for use as an anode material in lithium-ion batteries

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Abstract

Carbon materials were synthesized by the pyrolysis of acrylonitrile-butadiene-styrene terpolymer (ABS) under different heat treatment conditions. ABS decomposed in a rapid single-step reaction, which was completed around 600 °C. X-ray diffraction studies indicated a disordered carbon structure with a large number of single layer carbon sheets. It was found that varying the soak time, pyrolysis temperature and heating rate greatly affected the compositional, structural and electrochemical characteristics of the carbonaceous products. Charge–discharge studies of the product obtained by a 1 h pyrolysis at 600 °C at a heating rate of 20 °C/min exhibited first-cycle lithium insertion and deinsertion capacities of 825 and 564 mAh/g, respectively. Subsequent cycles showed a remarkable improvement in cycling efficiency with a 10th cycle efficiency of 100%.
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1. Introduction

The search for new anode materials that satisfy the current requirements of commercial lithium-ion batteries has been a long-standing goal of industrial and academic research. Numerous varieties of carbon materials have been studied for their use as an intercalation host in lithium-ion batteries. Non-graphitic carbon materials obtained from synthetic polymeric precursors have been of particular interest. For example, carbonaceous materials derived from phenolic resins were shown to possess improved electrochemical properties [1,2]: a carbon prepared from an epoxy novolac resin at 1000 °C exhibited a reversible capacity of 570 mAh/g, with minimal hysteresis in the cycling profiles, while a carbon prepared from a resol resin showed lithium insertion capacity of 550 mAh/g. Tokumitsu et al. [3] reported the synthesis of carbon materials from condensed polynuclear aromatics (COPNA) using pyrene cross-linked with dimethyl-*p*-xylene glycol (DMPXG). Hu and Chung [4] synthesized carbon materials from poly(acrylonitrile) (PAN) with a reversible capacity of 426 mAh/g. Also, according to Hu and Chung [4], a lower heating rate led to a higher reversible capacity. Saito et al. [5] reported improved charge–discharge characteristics and high power

capabilities with carbon fibers obtained by the pyrolysis of an active material bound in a thermosetting resin. A study on the effect of carbonizing conditions on the capacity of carbon materials derived from poly(*p*-phenylene) was also reported recently [6]. In another study, a reversible capacity of 320 mAh/g was reported for a carbon derived from quinoline pitch [7].

In this paper, we report the preparation and properties of disordered carbons synthesized from a polymeric precursor, acrylonitrile-butadiene-styrene terpolymer (ABS). The effect of pyrolysis conditions on the composition of the products, and their structural and electrochemical properties are discussed.

2. Experimental

Disordered carbons were prepared by pyrolyzing ABS at 600, 700, 800 and 900 °C in an argon atmosphere at a heating rate of 1 °C/min for a soak period of 1 h. For certain samples, a heating rate of 5 or 20 °C/min and a soak time 12 h were employed.

The thermal decomposition behavior of the precursor in argon was studied by thermogravimetric analysis (TGA) (Sieko SSC, 5000). The weight of the sample was typically 50 mg and the heating rate was 10 °C/min. Structural analysis was performed with a powder X-ray diffractometer using Cu K$_\alpha$ radiation (Siemens D-5000). Elemental analysis was done

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on a Perkin-Elmer CHN-2000 elemental analyzer. The products were coupled with lithium in 2032-type coin cells in an electrolyte of 1 M LiPF$_6$ in a 1:1 (v/v) mixture of EC and DEC. The electrodes were prepared as described elsewhere [8]. Galvanostatic charge–discharge studies on the cells were carried out at a 0.1C rate between 3.0 and −0.02 V on a multichannel battery tester (Maccor, Series 4000).

3. Results and discussion

3.1. Thermal studies

The thermogram (TG) and the differential thermogram (DTG) of the polymeric precursor are shown in Fig. 1. The TG shows a single-step decomposition process which starts at ~280 °C and is completed around 600 °C. There is no observable weight loss after 600 °C. The behavior is similar to the decomposition of PAN [4]. It is clear that the decomposition of the precursor is complete around 600 °C and that any changes that may occur beyond this temperature would be related to carbon layer organization.

3.2. Phase analysis

The X-ray diffractograms of the carbon products are shown in Fig. 2. The X-ray diffractograms show a typical disordered structure for all the carbons, with (0 0 2) and (1 0 0) peaks figuring prominently. The (0 0 2) peak shows a weak and broad profile, while the (1 0 0) peak grows as the pyrolysis temperature is increased, suggesting that the

materials prepared were amorphous. The X-ray diffractograms further show that the samples synthesized at the lower temperatures were mainly made up of single layer carbon sheets. Zheng et al. [1] made similar observations for carbon materials synthesized from epoxy resins. According to Lin et al. [2], the ratio of the height of the (0 0 2) Bragg reflection to that of the background, defined by the empirical parameter R, is a measure of the fraction of single layered carbon sheets in disordered carbons. The values of R were calculated from the X-ray data for the carbon samples. It was found to be the lowest for the carbons prepared at 600 °C, which indicates that the materials prepared at lower temperatures were made up of more single layers. According to Lin et al. [2], the materials with the largest single layer fraction will have the highest capacity for lithium insertion. Such layers can provide lithium accommodation sites on both sides. Because these single layers are not arranged in parallel, a large number of pores or voids also form between them [2]. According to Zheng et al. [1], who studied the pore structure of the carbon materials derived from phenolic resin using small angle X-ray scattering (SAXS), the pores between the randomly arranged graphene layers or carbon sheets provide extra lithium intercalation sites, resulting in capacities greater than the theoretical limit of 372 mAh/g possible with perfectly graphitic structures.

3.3. Elemental analysis

Results of elemental analysis of the carbonaceous products are shown in Table 1. Having already identified that a
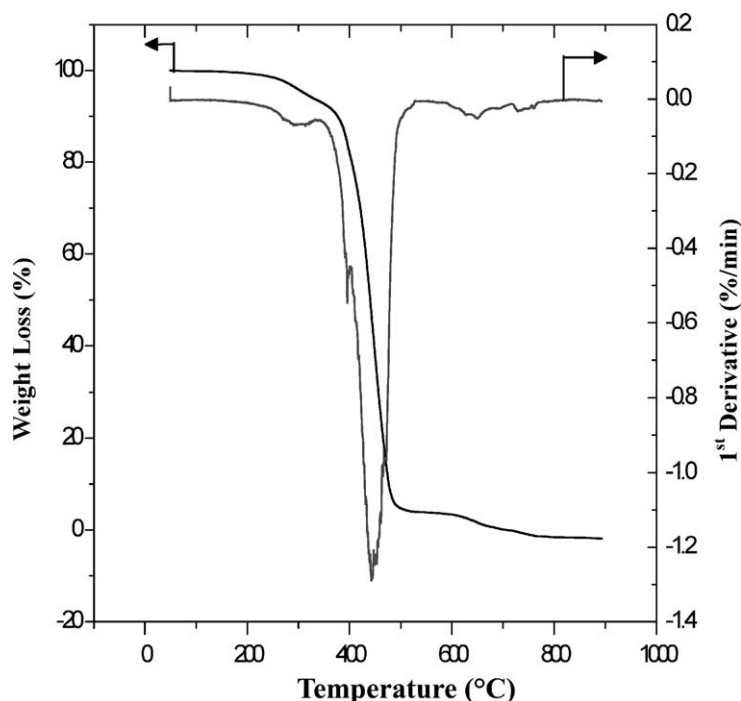

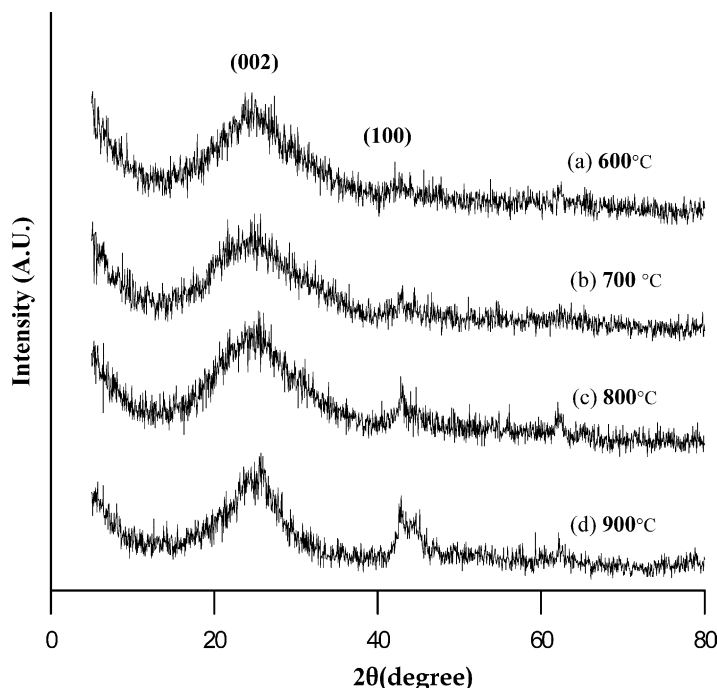Fig. 1. TG/DTG curves of the polymeric precursor, ABS.

Fig. 2. X-ray diffractograms of the carbon materials prepared at different pyrolysis temperatures.

pyrolysis temperature of 600 °C at a heating rate of 20 °C/min and soak time of 1 h resulted in a structure with a large number of single layer carbon sheets, the effects of varying the heating rate (5 and 1 °C/min) and soak time (12 h) were studied. It is clear from Table 1 that the hydrogen content was the greatest in the material prepared at 600 °C with a H/C ratio of 0.45. Varying the heating rate did not have much influence on the H/C ratio as shown in Table 1. It can also be seen that an increase in the soak or reaction time to 12 h led to a decrease in the H/C ratio.

3.4. Electrochemical studies

The charge–discharge studies showed that the materials prepared at lower temperatures delivered greater capacity, although with larger hysteresis, consistent with the results on carbons derived from other polymeric precursors [1,2].

For the carbon material prepared at 600 °C at a heating rate of 20 °C/min with a soak time of 1 h, the first-cycle lithium insertion and deinsertion capacities were 825 and 564 mAh/g, respectively, accounting for an irreversible capacity of 32%. The coulombic efficiency improved upon cycling. In the 10th cycle, the charge density of this product was 410 mAh/g, with coulombic efficiency of 100%. A comparison of the capacity values for the carbon materials prepared at different pyrolysis temperatures is shown in Table 2, which illustrates that the insertion and deinsertion capacities dropped when the pyrolysis temperature was increased. The hysteresis in the charge–discharge profiles also diminished simultaneously. The first-cycle irreversible capacities also generally increased with the pyrolysis temperature. The increased capacity of the materials prepared at the lower temperatures may be ascribed to the presence of hydrogen. According to Zheng et al. [9], the amount of lithium that

Table 1
Elemental analysis of the disordered carbon materials prepared under different conditions

Element	Weight percent (%)								
	Pyrolysis temperature[a]				Heating rate[b]			Soak time[c]	
	900 °C	800 °C	700 °C	600 °C	1 °C/min	5 °C/min	20 °C/min	1 h	12 h
N	3.12	2.79	3.00	3.19	4.60	4.10	3.19	4.10	3.93
C	81.28	77.87	77.50	77.93	82.92	82.16	77.93	82.16	82.04
H	1.26	1.55	2.19	2.97	3.21	3.04	2.97	3.04	2.53
H/C	0.19	0.23	0.34	0.45	0.46	0.44	0.45	0.44	0.37

[a] Heating rate: 20 °C/min; soak time: 1 h.
[b] Pyrolysis temperature: 600 °C; soak time: 1 h.
[c] Pyrolysis temperature: 600 °C; heating rate: 5 °C/min.

Table 2
Insertion and deinsertion capacities of carbon materials prepared under different conditions

Cycle no.	Capacity (mAh/g)																	
	Pyrolysis temperature[a]								Heating rate[b]						Soak time[c]			
	600 °C		700 °C		800 °C		900 °C		1 °C/min		5 °C/min		20 °C/min		1 h		12 h	
	IC	DC	IC	DC	IC	DC	IC	DC	IC	DC	IC	DC	IC	DC	IC	DC	IC	DC
1	825	564	902	560	635	376	608	401	1133	619	1198	639	825	564	1198	639	606	307
2	571	528	546	532	382	368	399	384	592	527	615	554	571	528	615	554	360	319
3	528	505	524	519	367	359	383	374	507	479	532	505	528	505	532	505	357	323
5	480	471	505	504	351	349	365	359	440	431	442	435	480	471	442	435	338	327
10	409	410	474	474	332	331	344	342	361	360	369	368	409	410	369	368	317	300

IC: insertion capacity; DC: deinsertion capacity.

[a] Heating rate: 5 °C/min; soak time: 1 h.

[b] Pyrolysis temp.: 600 °C; soak time: 1 h.

[c] Pyrolysis temp.: 600 °C; heating rate: 5 °C/min.

can be inserted in a carbon material is directly related to its hydrogen content. Our results vindicate the above conclusion in that the highest H/C ratio was obtained for the material prepared at 600 °C. As the pyrolysis temperature was increased, there was a steady decrease in both the H/C ratio (Table 1) and the insertion capacity.

Low-temperature synthesized disordered carbons consist of randomly arranged single layers of carbon sheets resembling "falling cards" [10] between which exist tiny pores or voids. The number of single sheets of carbon is related to the empirical R value. In carbons with small R values, there is a preponderance of unorganized single carbon sheets. The R values were the lowest for the materials prepared at 600 °C, which indicate the presence of more single layers of carbons in these materials and, hence, more pores or voids. As the pyrolysis temperature was increased, the R values were found to decrease, indicating a decrease in the number of single layers of carbon, which tend to get organized at elevated temperatures. The decrease in the value of R indicates a diminution in the population of pores and voids available for lithium occupation. A large distribution of such sites would result in large values for lithium intake. When the number of single carbon layers decreases, as in the case of materials prepared at higher temperatures, lithium intercalation is limited to those regular sites as obtained in graphitic structures, with a tendency towards capacity attenuation. Because the insertion–deinsertion processes in such structures are nearly similar to those in graphites, the hysteresis in the charge–discharge profiles is small.

When the materials were prepared at 600 °C at different heating rates, there were remarkable differences in the deinsertion capacities (Table 2). The material prepared at a heating rate of 5 °C/min showed a first-cycle insertion capacity of 1198 mAh/g and a deinsertion capacity of 639 mAh/g, with a coulombic efficiency of 53%. When the heating rate was reduced to 1 °C/min, the first-cycle deinsertion capacity decreased to 619 mAh/g. Thus, the products from pyrolysis at heating rates of 5 and 1 °C/min, despite possessing high deinsertion capacities (639 and

619 mAh/g, respectively), are unsuitable for device applications because of their unacceptably high irreversible capacities (47 and 45%, respectively). Fig. 3 illustrates the effect of the heating rate on the charge–discharge behavior of carbons prepared by 1 h pyrolysis at 600 °C. Similar observations of high capacities have been reported for carbons derived from PAN at low heating rates [11]. At low rates of heating, the evolution rates of the decomposition
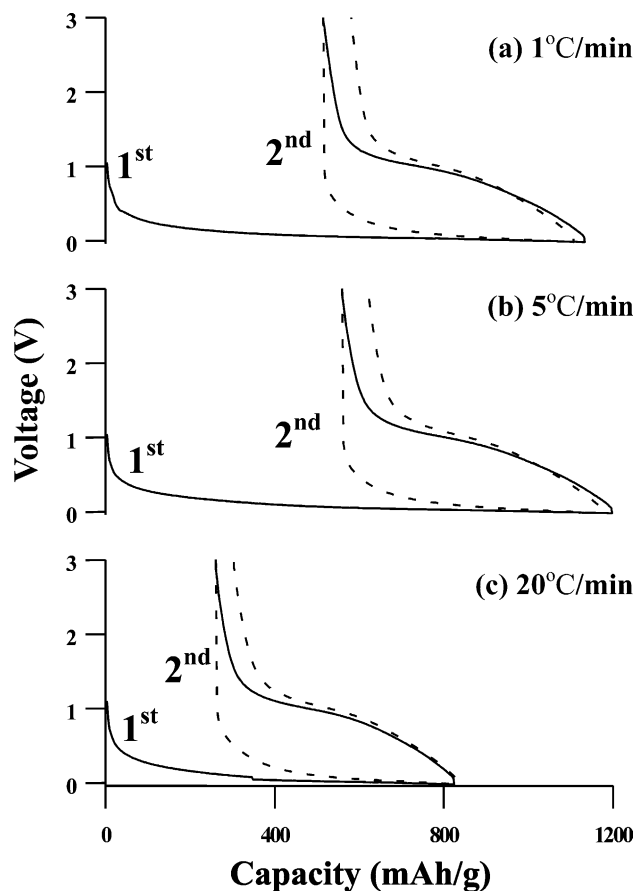
Fig. 3. Charge–discharge characteristics of carbon materials prepared at different heating rates (pyrolysis temperature: 600 °C; soak time: 1 h).

products would also decrease, producing in the process a more uniform nanoporous material. Such a nanoporous structure could provide a large number of sites that can accommodate lithium. However, the lower heating rates would also prolong the time to reach the set temperature (600 °C), during which period a slow alignment of the single layers could take place and reduce lithium intake capacity. Thus, two processes, one aiding the proliferation of lithium accommodation sites and the other screening away such sites, occur in parallel. The net capacity is determined by which process is dominant. Such a visualization of the pore-formation and carbon layer alignment occurring simultaneously would explain the highest capacities observed at the intermediate heating rate (5 °C/min). However, for the carbon material synthesized from PAN, Wu et al. [11] found the highest capacity at the lowest heating rate (0.5 °C/min). It is clear, therefore, that the conditions for the pyrolytic preparation of carbon materials suitable for lithium batteries must be arrived at with care.

We also investigated the effect of increasing the soak time on the deliverable capacity. For this, the soak time was increased to 12 h at 600 °C at a heating rate of 5 °C/min. This resulted in a decrease in capacity (first-cycle deinsertion capacity: 307 mAh/g) (Table 2). The first-cycle irreversible capacity for this sample was an inordinately high 49%. An analysis of Table 2 would indicate that based on the lowest first-cycle irreversible capacity and the 10th cycle deinsertion capacity, the optimum pyrolysis conditions for the preparation of carbons from ABS would be pyrolysis at 600 °C for 1 h at a heating ramp of 20 °C/min. Wu et al. [11] suggest that pores are generated by the release of such gases as HCN and CH$_4$. During prolonged heating, some pores may combine and some may even disappear. The evolution of these gases would also mean a reduction in the H/C ratio of the product. Thus, the decrease in capacity may be attributed to the lower H/C ratio, fewer nanopores and increased alignment of the single carbon layers during the extended heating period.

Fig. 4 illustrates the variation of the capacity with cycle life for all the carbonaceous products. It can be seen that all the products gave very high coulombic efficiencies (close to 100%) in the 10th cycle. However, the capacity fade up to the 10th cycle was found to decrease with the heat treatment temperature (1 h, 20 °C/min), the typical values being 27.3, 15.4, 12.0 and 14.7% for 600, 700, 800 and 900 °C, respectively. The capacity fade also decreased with the heating rate. For example, when the heating rate was increased from 1 to 20 °C/min (600 °C, 1 h), the capacity fade decreased from 41.8 to 27.3% over 10 cycles. However, the most remarkable reduction in capacity fade was achieved when the soak time was increased from 1 to 12 h (600 °C, 5 °C/min), which reduced the capacity fade from 42.4 to a mere 2.3%.

Thus, it is clear that the capacity of carbon materials depends on the pyrolysis temperature, heating rate and soak time. The higher insertion capacities of the materials with
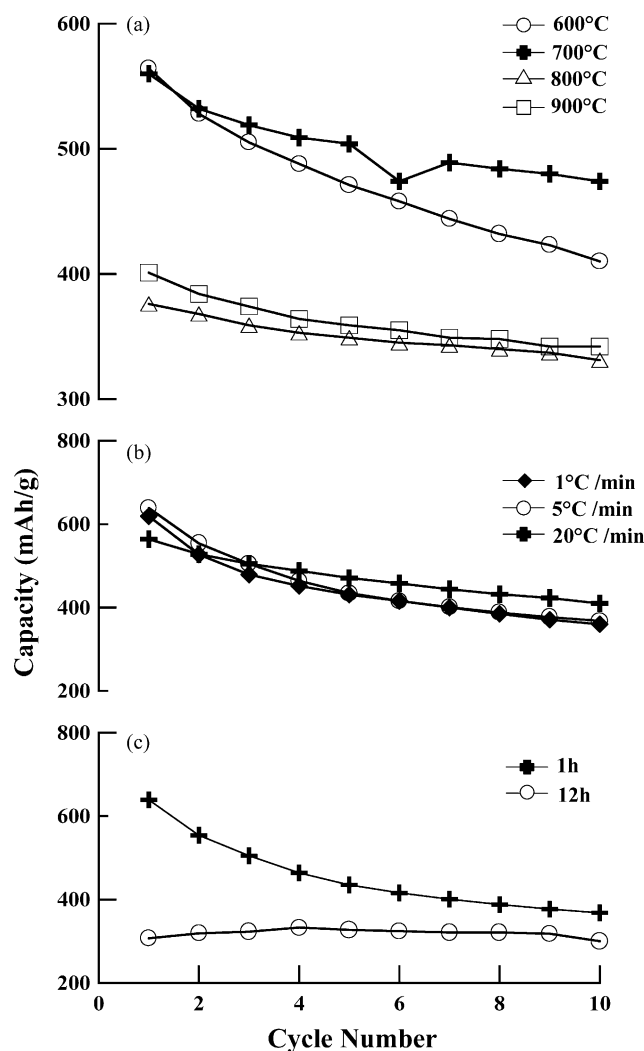

Fig. 4. Cycling behavior of the carbonaceous products as a function of (a) the pyrolysis temperature (heating rate: 20 °C/min; soak period: 1 h); (b) the rate of heating (pyrolysis temperature: 600 °C; soak period: 1 h); (c) the soak period (pyrolysis temperature: 600 °C; heating rate: 5 °C/min). Charge–discharge at 0.1C rate between 3.00 and −0.02 V.

higher hydrogen content can be explained using the polarized-charge model proposed by Wang et al. [6]. According to their model, the carbonization process changes the benzene rings in the precursor to condensed ring compounds and graphite crystallite edges with hydrogen atoms [6]. Because of its high electronegativity, the oxygen in the electrolyte molecules further polarizes the C–H covalent bond [6], resulting in the oxygen atoms moving closer to the hydrogen of the C–H bond [6]. What follows is a partial transfer of the negative charge to the carbon, which gets distributed in the structure by an inductive effect [6]. The insertion energy required for inserting lithium ions into the carbon layer is thereby decreased [6]. According to above model, the capacity is mainly determined by the hydrogen content of the carbon materials. Another explanation proposed for higher lithium capacity of carbons prepared at different temperatures is based on the bonding between

lithium and carbon [12]. Recently, Sandi and co-workers [13] attributed the high lithium insertion capacity of products obtained by the carbonization of pyrene in the galleries of aluminum-pillared bentonite and sepiolite clays [14,15] to carbon structures with curved lattices. Based on their molecular orbital calculations of lithium complexes of buckminster fullerene, C_{60} [16], Sandi and co-workers [13] suggested that curved carbon structures provided bowl-shaped cavities, which facilitated a close approach of lithium, accounting for lithium insertion levels higher than that in graphitic structures.

4. Conclusions

Carbon materials were synthesized from poly(acrylonitrile-*co*-butadiene-*co*-styrene) under different pyrolytic conditions. Thermal studies of the precursor showed a rapid single-step decomposition reaction occurring below 600 °C. X-ray diffraction studies showed that all the pyrolytic products were highly disordered. The low values of the empirical factor R revealed the presence of large numbers of single layers of carbon sheets for the material prepared at 600 °C. The H/C ratio value was also the highest for the material pyrolyzed at 600 °C. An increase in the heating rate or soak time led to a decrease in the first-cycle deinsertion capacity. The higher H/C ratio, and the greater presence of nanopores and single layer carbons are supposed to enhance the lithium intake in the low-temperature pyrolyzed materials. Pyrolysis of ABS at 600 °C for 1 h at a heating ramp of 20 °C/min gave a first-cycle irreversible capacity of 32%. Further, the coulombic efficiency improved with cycling: in the 10th cycle it was 100% with a lithium deinsertion

capacity of 410 mAh/g. A polarized-charge model was used to describe the enhanced electrochemical characteristics for the materials containing hydrogen.

Acknowledgements

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