# Effect of mixing sequences on the electrode characteristics of lithium-ion rechargeable batteries

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## Abstract

Measurements are made of the viscosity of a liquid-phase slurry by varying the mixing sequences, during the preparation of a positive electrode for a lithium-ion rechargeable battery. The slurry consisted of active material powder, conductive agent powder, polymer binder solution, and liquid solvent. The slurry viscosities are analyzed through consideration of the suspension rheology. The half-cell characteristics of a positive electrode prepared from the slurry are also investigated. Although the same materials and the same contents are used, the slurries show different scales of viscosity that reflect different dispersion states of the solid particles. Accordingly, the half-cell exhibits different discharge characteristics. The best discharge capacity, in terms of stability during repeated cycle, is obtained by dry-mixing the powders and then adding binder solution and solvent in sequence. © 1999 Elsevier Science S.A. All rights reserved.

## 1. Introduction

Since the first commercialization by Sony Energytech [1,2] in the early 1990s, lithium-ion battery (LIB) has become a major product which dominates the market for small rechargeable batteries. The LIB is manufactured through a series of processes, namely, electrode preparation, cell assembly, grading and formation, safety evaluation. Now, with the help of competitive research activities by batterymakers, many details of the technology are established, i.e., from material selection through production processes to quality control systems.

It is well-known that in the preparation of electrodes for LIBs, lithium alkali metal oxides such as $LiCoO_2$, $LiMn_2O_4$ and $LiNiO_2$ are used as positive active materials, and carbons or graphites as negative active materials. Usually, the active material is mixed with a fine carbon powder as conductive agent and a polymer binder to enhance the adhesion between particles. Because the choice of such materials can influence greatly the performance of the LIB, many studies of the material properties have been performed (refer to representative works for positive [3] and negative [4] active materials, electrolyte solution [5,6], and also to recent reviews for materials [7–9] and LIBs [10–13]). As a result, material optimization for the LIB is firmly established by each maker. In addition to the effects of material selection, the processing methods may also affect LIB performance and thus, are worthy of examination.

As a starting point for the study of processing technology, the effect of the mixing sequence of source materials on the electrode characteristics may be investigated. It has been reported [14] that the life cycle can be increased threefold by changing the mixing method for the preparation of LIB negative electrodes. It has also been suggested [15] that the mixing ratio of particle sizes might be an important factor in determining the electrical capacity of LIBs. Thus, it is expected that the cell may exhibit different characteristics by a change in mixing sequence for

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positive electrode. In fact, some factors of the mixing process, such as mixing method [16] and content ratio [17] of positive active material to conductive agent, are known to be determinants of LIB performance. Therefore, in the present work, we have examined the positive half-cell characteristics which are influenced by the mixing sequence. To achieve this, we have prepared slurries with varying mixing sequences, applied them to aluminum foil as a current-collector to make positive electrodes, made half-cells with lithium metals as counter- and reference-electrodes, and then tested the cell by using charge–discharge cycling equipment.

## 2. Experimental

LiCoO$_2$ (Nippon Chem. Ind.) was used as a positive active material, graphite powder (Nihon Graphite) as a conductive agent, 12 wt.% poly(vinylidene fluoride) (PVDF) solution (Kureha Chem. Ind.) in *N*-methyl-2-pyrrolidone (NMP) as a binder solution, and NMP (Aldrich Chemical) as a solvent. The weight ratio of each constituent was LiCoO$_2$:graphite:PVDF = 89:6:5. The solid content was fixed at 66.7% for all methods of mixing and thus, the weights of the materials were LiCoO$_2$ powder 100.0 g, graphite powder 6.74 g, binder solution 46.83 g, and liquid solvent 14.97 g.

The particle properties expected to influence the mixing process are size, specific gravity, specific surface area, and solvent uptake. These are shown in Table 1. The values of apparent density and solvent uptake, which were measured directly by following the Japanese Industrial Standard (JIS) R7222 (physical testing method of high-purity graphite materials), are also shown in Table 1.

The mixing sequence used to prepare slurries for the positive electrode was based on the four methods given in Fig. 1. For method 1, the conductive agent and the binder solution were added simultaneously and then placed under vacuum (25 in Hg) for 90 min at room temperature to allow the powder particles to absorb the liquid. Active material powder and liquid solvent were then added with mechanical stirring at 1000 rpm for 30 min. The viscosity was monitored by means of a Brookfield rotary viscometer until it reached a stabilized value. Method 2 was the same
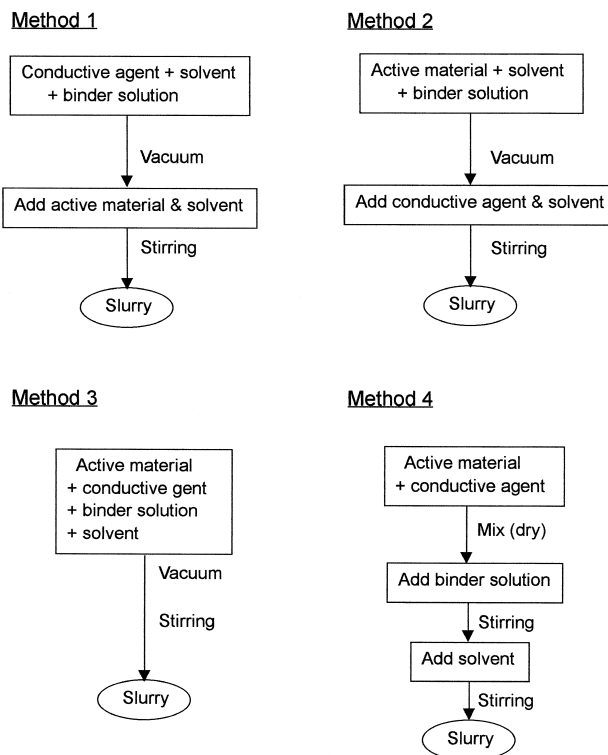


Fig. 1. Four methods of preparing slurry mixtures.

as method 1 but the addition points of conductive agent and active material were interchanged. Application of a vacuum for 150 min was required for method 2. In method 3, all the source materials were added simultaneously. The mixture was then placed under vacuum for 180 min, the mechanical stirring was started and the viscosity was monitored. In method 4, the active material and the conductive agent were pre-mixed under a dry atmosphere by slow stirring at 50 rpm for 60 min. The binder solution was then added and the stirring speed increased to 1000 rpm. The resulting mixture was placed under vacuum for 30 min, liquid solvent was added, and the viscosity monitored.

The slurries were applied uniformly on one side of an aluminum foil (20 μm thick) by using a knife coater (gap 150 μm) and then dried at 140°C in chamber for 20 min to evaporate NMP and to produce positive electrodes (cathodes). The positive electrodes were pressed through a doubleroll press (gap 130 μm, 1000 kg cm$^{-1}$, 100°C) to obtain electrodes with a high packing density.

Positive half-cells were prepared within a dry room under dehumidifying conditions (dew point below −60°C). Jelly-roll type half-cells (see Fig. 2) were obtained by layering the positive electrode sheet (size 30 mm × 170 mm) and lithium metal sheets (size 40 mm × 210 mm and 40 mm × 100 mm for counter- and reference-electrodes, respectively), which were separated by four sheets of separator (polypropylene/polyethylene/polypropylene, Nitto Denko). The electrolyte solution was lithium hex-

Table 1
Physical properties of powder samples

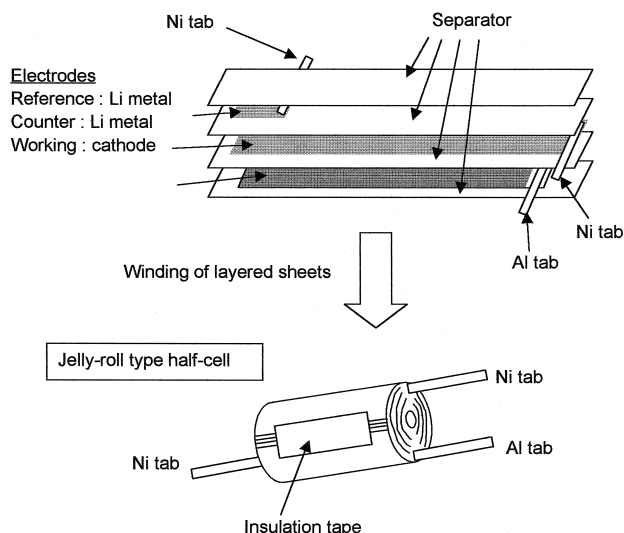|  | LiCoO$_2$ | Graphite |
| --- | --- | --- |
| Average particle diameter (μm) | 5 | 2 |
| BET surface area (m$^2$ g$^{-1}$) | 0.4–0.9 | 200–270 |
| Specific gravity | 4.2 (4.11[a]) | 2.17[a] |
| Apparent density (g cm$^{-3}$) | 2.1[a] | 0.12 (0.41[a]) |
| Solvent uptake (ml NMP g$^{-1}$) | 0.28[a] | 1.9[a] |

[a]Measured in present study.

Fig. 2. Schematic illustration of half-cell construction.

afluorophosphate (1 M LiPF$_6$) dissolved in an ethylene carbonate (EC)–diethyl carbonate (DEC)–dimethyl carbonate (DMC) (1:1:1 by volume) mixture. Three half-cells were prepared for each method. The half-cells were cycled about 45 times by using a cycler (Toyo Systems) under constant-current (CC) charging (0.2 C) followed by con-

stant voltage (CV) (4.3 V cut-off), and under CC discharging (0.2 C) followed by a 2.7-V cut-off.

## 3. Results and discussion

### 3.1. Slurry viscosity

It is well-known that viscosity control is important in determining the optimal dispersion state of a slurry. Slurry viscosity can be measured from the onset of liquidization, e.g., the step of wetting, and eventually reaches a stabilized value which does not change with time. The stabilized viscosity may be changed by the varying mixing sequence because the diffusion of the liquid component into the internal region (void or pore) of solid particles can be affected by the mixing method. The degree of mixing depends on particle size, particle-size distributions, specific surface area, solvent uptake, etc.

The variation in viscosity for each mixing method with time is shown in Fig. 3. The curve in Fig. 3a is that for method 1, i.e., adding active material powder after equilibration of the conductive agent, binder, and solvent (equilibration means the state of constant liquid level in the vessel) whereas the curve in Fig. 3b is for method 2, i.e.,
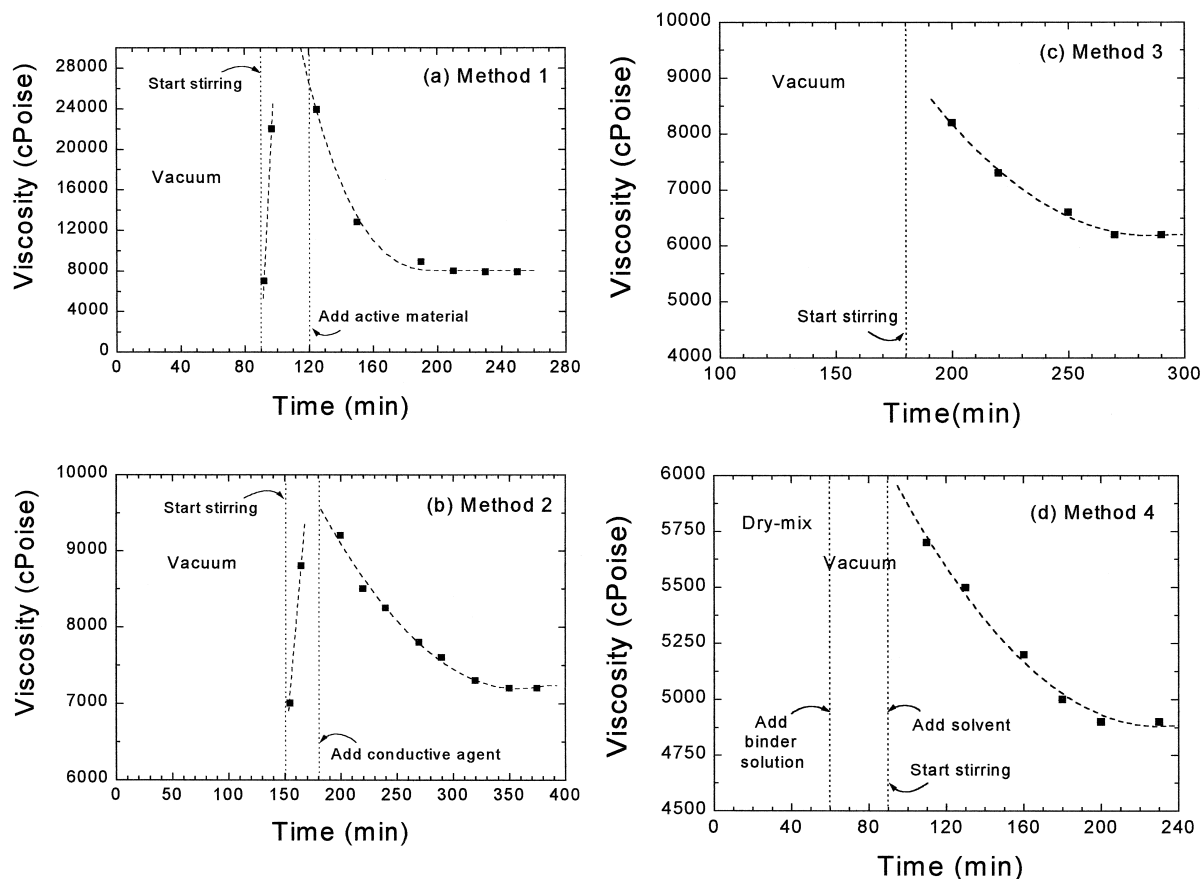


Fig. 3. Viscosities measured for each mixing sequence: (a) method 1; (b) method 2; (c) method 3; (d) method 4.

Table 2
Stabilized viscosities and times required from start of stirring

| Method | Viscosity (cP) | Time (min) | Pre-vacuum time (min) |
|---|---|---|---|
| 1 | 8100 | 100 | 30 |
| 2 | 7250 | 200 | 30 |
| 3 | 6200 | 90 | 180 |
| 4 | 4800 | 130 | 30[a] |

[a] Pre-vacuum is followed by dry-mixing of solid powders.

adding conductive agent after active material, binder, and solvent. Method 1 displays a larger change in viscosity and obtains a stable value in a shorter time compared with method 2 (see also Table 2). The liquid absorption of active material in method 1 may be insufficient because the conductive agent, which has a specific surface area 350 times greater than that of the active material, already contains a large amount of liquid. With method 1, therefore, the liquid component entrapped in the internal space of conductive agent does not simply flow out, while with method 2, the active material with small specific area may release the liquid easily. In addition, the time required for viscosity stabilization from the start of stirring depends on the surface area of the powders added subsequently. Method 2 requires more time than method 1 to reach a stable viscosity because the conductive agent has a large surface area.

The curve for method 3 (Fig. 3c), in which all the source materials are added simultaneously, shows that although the pre-evacuating time is very long, the time to reach a stable viscosity is the shortest. This is the case of absorbing liquid by active material and conductive agent concurrently, and that of stirring under conditions in which the active material and the conductive agent share an amount of liquid independently, which corresponds to the specific surface area of each powder. Contrary to these observations, Fig. 3d shows that method 4 takes a considerable time to stabilize the viscosity but the value of the stable viscosity is the lowest. Thus, even if the same materials and the same contents are added, the levels of the stabilized viscosity are different for different mixing sequences. That is to say, different mixing conditions can induce a deviation in the degree of absorbing liquid and the effect can be reinforced when using two powders with highly different specific surface areas and liquid uptakes.

### 3.2. Suspension rheology

Suspension rheology treatment of the flow properties of particle-filled solutions can be applied to the present slurry system. In suspension rheology (refer to review of Metzner [18]), the slurry viscosity $\mu$ or relative viscosity $\mu$ (ratio of slurry viscosity to liquid viscosity $\mu_0$) depends strongly on the volume fraction $\phi$ of the solid components and on the maximum volume fraction of solids, size, shape, modality

or size distribution of the particles. The present slurry system can be regarded as two solid particles (active material and conductive agent) dispersed in a polymer solution and thus, can be compared with the results of viscosity changes [19] in a bimodal suspension system. The basic data calculated from Table 1 are: (i) the volume fraction of the solid components $\phi = 0.25$ to $0.60$ (by adopting a simple additivity rule from the values of specific gravity and apparent density give in the table); (ii) the volume fraction of the small particles in the total solids $\phi_s = 0.115–0.257$; (iii) the particle-size ratio $r = 2/5 = 0.4$. The liquid viscosity of 650 cP is based on the polymer solution including the residual solvent. Ranges are given for $\phi$ and $\phi_s$ because the setting of limits between the fully absorbed state of liquid into the internal region of the solid particles and the unabsorbed state, corresponds to the specific gravity and the apparent density, respectively.

The calculated results, using the bimodal suspension model [19,20] and applying the slurry condition outlined above, are presented in Fig. 4. The measured slurry viscosities and the stabilized values (horizontal lines for methods 1–4 from top to bottom) fall within the region bounded by $\phi_s = 0.115$ to $0.257$ and $\phi = 0.25$ to $0.60$. A lower amount of liquid is absorbed in the upper part of the viscosity region. The stabilized viscosities are positioned in the lower part of the region and reflect the amount of liquid absorbed. Thus, it is concluded that method 4 gives the highest level of liquid absorption and the best dispersion state.
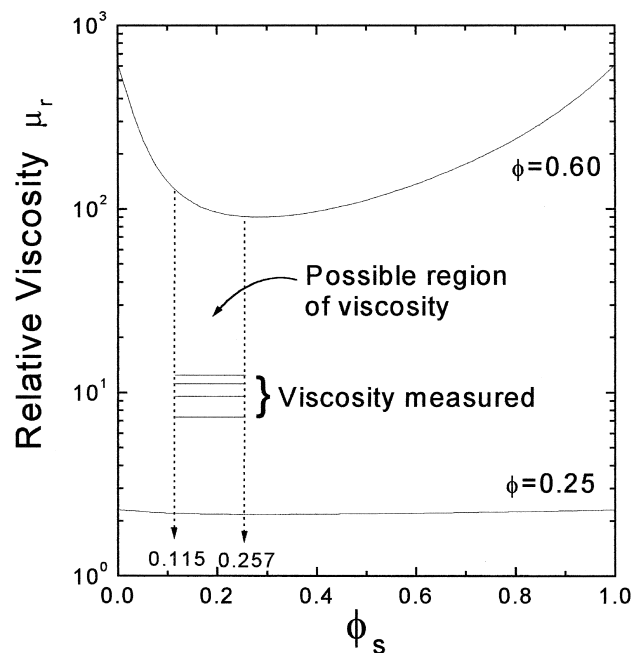


Fig. 4. Relative viscosity vs. volume fraction of small particles in total solids. Solid curves obtained by suspension model [19,20] of bimodal particle distribution. Lines of viscosity measured are for methods 1 to 4 from top to bottom.

Table 3
Thickness changes of electrodes

| Method | After coating ($\mu$m) | After pressing ($\mu$m) | Degree of compression[a] (%) |
|---|---|---|---|
| 1 | 121–125 | 97–101 | 19.5 |
| 2 | 124–130 | 100–105 | 18.9 |
| 3 | 121–123 | 97–101 | 18.9 |
| 4 | 118–120 | 92–96 | 21.0 |

[a]For average thickness: (before pressing − after pressing)×100/(before pressing).

### 3.3. Electrode surface

The changes in thickness of electrodes after coating and roll-pressing are shown in Table 3. The morphology of the electrode surface prepared by method 4 is displayed in Fig. 5. In the electrode surface after coating and drying, small particles of conductive agent are fixed between the active material particles. In addition, many voids, both in plane and in depth, are easily observed. Pressing the electrode increases the packing density in the electrode surface. The electrode prepared by method 4 exhibits the highest compression ratio (21%) but this does not deviated much from that obtained with the other methods.
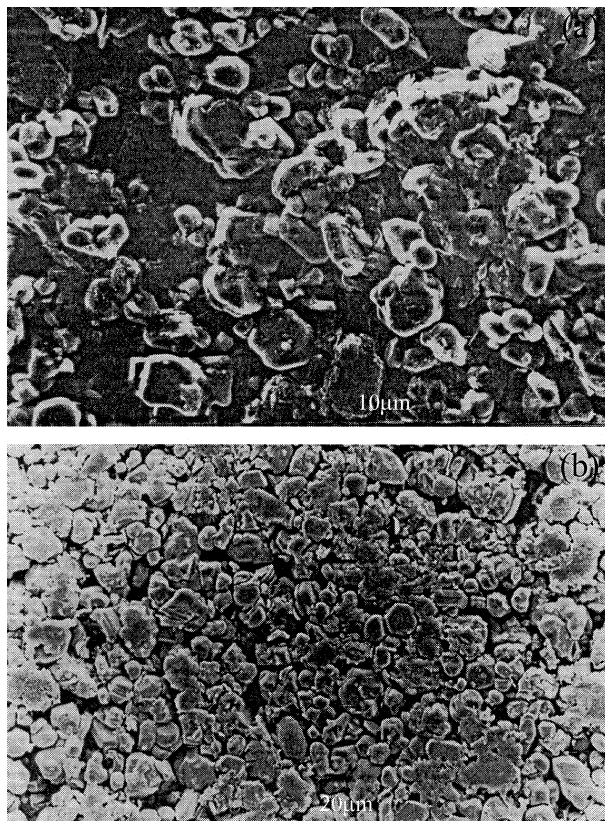
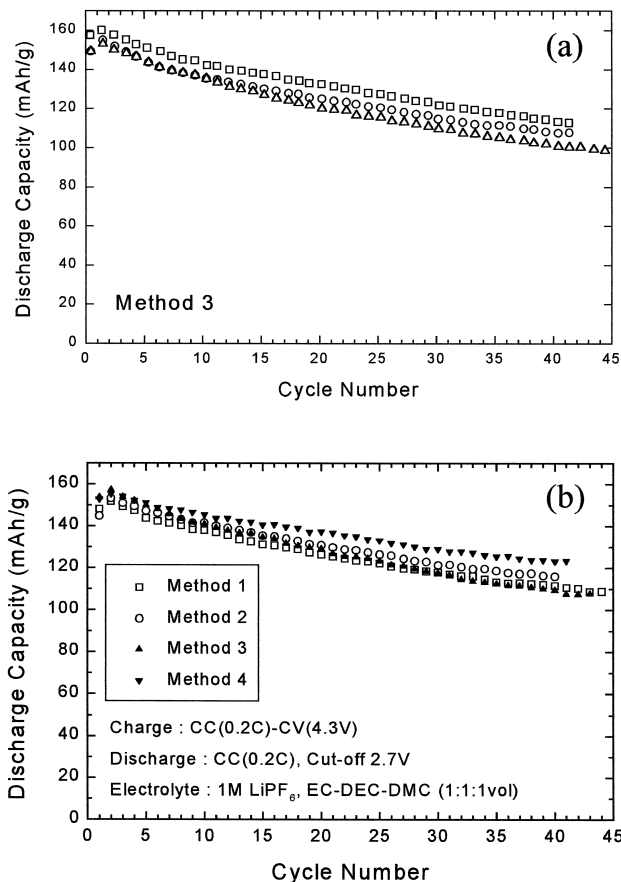Fig. 5. Electron micrographs of positive electrode surface (method 4): (a) before and (b) after roll-pressing.

Fig. 6. Specific discharge capacities of $LiCoO_2$ /Li half-cells prepared by (a) method 3 (for three cells tested) and (b) methods 1 to 4 (averaged over three cells for each method).

### 3.4. Discharge characteristics

The change in discharge capacity with cycling for three half-cells using method 3 is shown in Fig. 6a. The averaged values over three half-cells for each method are presented in Fig. 6b. For methods 1, 2, and 4, the half-cells exhibit the same discharge capacities, but for method 3, the capacities deviate by 7 mA h g$^{-1}$ on the first cycle and by about 20 mA h g$^{-1}$ on the 40th cycle. This is due to a lack of local uniformity in the dispersion state of slurry prepared by method 3. Method 4 produces the most stable capacity, i.e., on the 40th cycle, about 80% of initial capacity is retained. This is because method 4 is the most efficient means of achieving the highest dispersion state of the slurry.

### 4. Concluding remarks

The present study demonstrates that the mixing sequence in slurry preparation can affect the performance of LIBs, particularly the stability of discharge capacity on cycling. The most beneficial slurry dispersion state can be obtained by pre-mixing dry particles which have large

differences in specific surface area, and by adding the binder solution and liquid solvent in sequence. The present study has been performed only on a laboratory scale. The results may change when using a pilot-scale mixer to obtain a greater amount of slurry or a micro-mixer to achieve high-precision. These cases should be also examined to determine their own optimum conditions of mixing.

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