

## Supporting Information

### Phase Behaviors and Ion Transport Properties of LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>/Sulfone Binary Mixtures

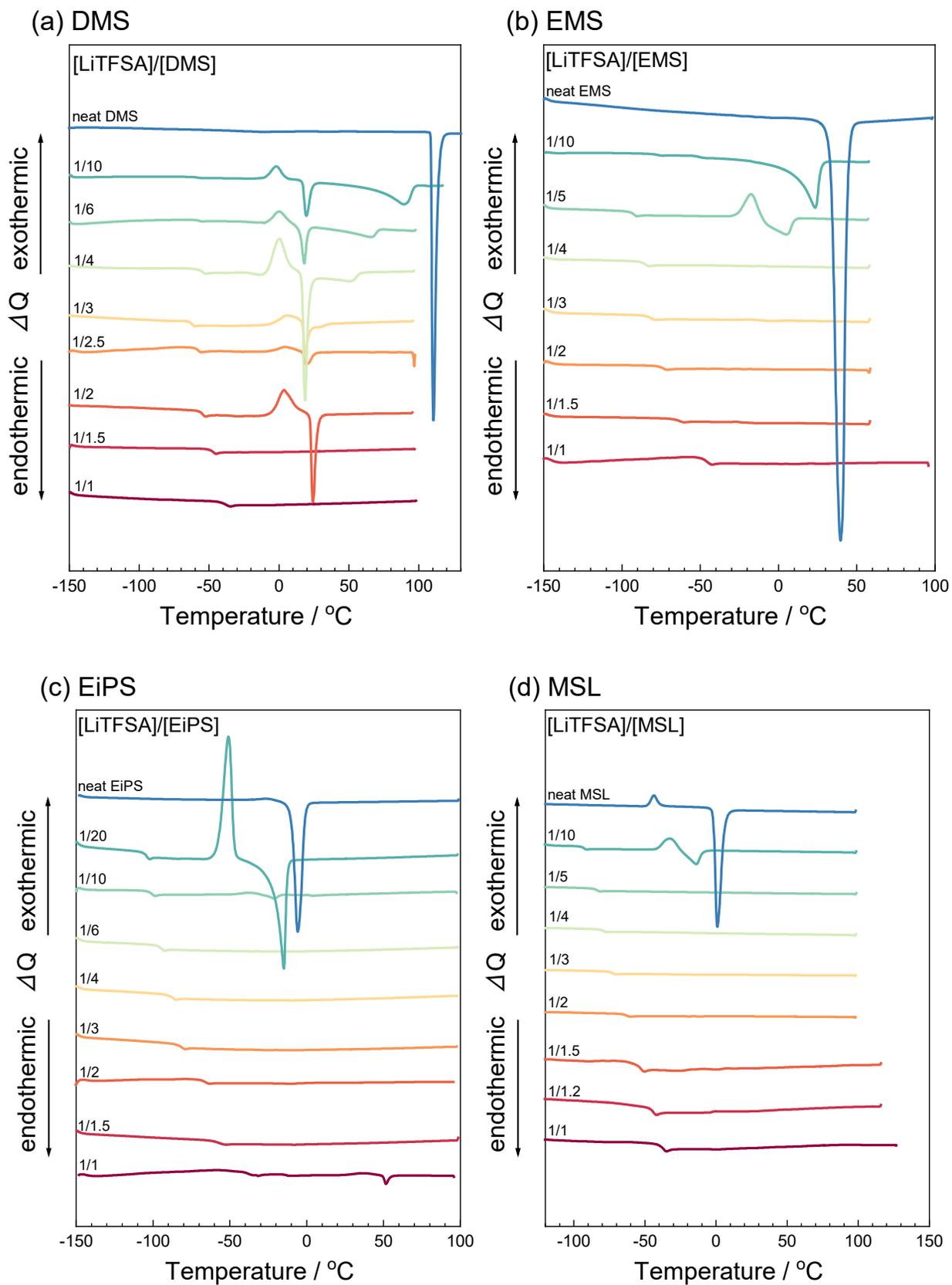
Ryoichi TATARA,<sup>a,†</sup> Yosuke UGATA,<sup>a,b</sup> Shuhei MIYAZAKI,<sup>a</sup> Natsuki KISHIDA,<sup>a</sup>  
Shohei SASAGAWA,<sup>a</sup> Kazuhide UENO,<sup>a,b</sup> Seiji TSUZUKI,<sup>b</sup> Masayoshi WATANABE,<sup>b</sup>  
and Kaoru DOKKO<sup>a,b,\*</sup>

<sup>a</sup> Department of Chemistry and Life Science, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

<sup>b</sup> Advanced Chemical Energy Research Center, Institute of Advanced Sciences, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

<sup>†</sup>Present address: Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan

\*Corresponding author: dokko-kaoru-js@ynu.ac.jp



**Figure S1.** DSC curves of (a) LiTFSA/DMS, (b) LiTFSA/EMS, (c) LiTFSA/EiPS, and (d) LiTFSA/MSL mixtures.

**Table S1.** Crystallographic data for [LiTFSA]/[EiPS]=1/1 and [LiTFSA]/[MSL]=1/1.

|  | [LiTFSA]/[EiPS]=1/1   | [LiTFSA]/[MSL]=1/1  |
|--|---|---|
| Chemical formula                                   | C <sub>14</sub> H <sub>24</sub> F <sub>12</sub> Li <sub>2</sub> N <sub>2</sub> O <sub>12</sub> S <sub>6</sub> | C <sub>14</sub> H <sub>20</sub> F <sub>12</sub> Li <sub>2</sub> N <sub>2</sub> O <sub>12</sub> S <sub>6</sub> |
| Formula weight                                     | 846.59  | 842.56  |
| Crystal system                                     | monoclinic  | orthorhombic  |
| Space group  | P 1 21/c 1  | P n a 21  |
| <i>a</i> / Å                                       | 18.9850(9)  | 17.8545(10)   |
| <i>b</i> / Å                                       | 8.7718(4)   | 12.6864(7)  |
| <i>c</i> / Å                                       | 21.8241(12)   | 14.6399(8)  |
| $\alpha$ / °                                       | 90  | 90  |
| $\beta$ / °  | 111.777(6)  | 90  |
| $\gamma$ / °                                       | 90  | 90  |
| <i>V</i> / Å <sup>3</sup>                          | 3375.1(3)   | 3316.1(3)   |
| <i>Z</i>   | 4   | 4   |
| <i>D</i> <sub>calc</sub> / g cm <sup>-3</sup>      | 1.666   | 1.688   |
| $\mu$ / mm <sup>-1</sup>                           | 0.524   | 0.533   |
| Temp. / K  | 223   | 223   |
| Reflections collected                              | 65601   | 29957   |
| Independent reflection, <i>R</i> <sub>int</sub>    | 9251, 0.0358  | 8471, 0.0215  |
| <i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )] | 0.0467  | 0.0455  |
| <i>wR</i> <sub>2</sub> (all data)                  | 0.1534  | 0.1310  |
| Goodness of fit                                    | 0.932   | 1.030   |
| Largest residual density / eÅ <sup>-3</sup>        | 0.659, -0.443   | 0.568, -0.319   |

The crystallographic information files (cifs) for [LiTFSA]/[EiPS]=1/1 and [LiTFSA]/[MSL]=1/1 were deposited in the Cambridge Structural Database (CSD) as CCDC 2224170 and 2224171, respectively.

**Table S2.** Viscosity ( $\eta$ ), density ( $\rho$ ), LiTFSA concentration ( $c$ ), ionic conductivity ( $\sigma$ ), and diffusivity ( $D$ ) of the LiTFSA–MSL electrolytes at 30 °C.

| [MSL]/[LiTFSA] | $\eta$<br>mPa s | $\rho$<br>g cm <sup>-3</sup> | $c$<br>mol dm <sup>-3</sup> | $\sigma$<br>mS cm <sup>-1</sup> | $D_{\text{Li}}$                                  | $D_{\text{sol}}$ | $D_{\text{TFSA}}$ |
|----------------|-----------------|------------------------------|-----------------------------|---------------------------------|--|------------------|-------------------|
|                |                 |                              |                             |                                 | 10 <sup>-7</sup> cm <sup>2</sup> s <sup>-1</sup> |                  |                   |
| 3              | 176             | 1.42                         | 2.06                        | 0.75                            | 0.82   | 0.87             | 0.74              |
| 4              | 91              | 1.38                         | 1.67                        | 1.18                            | 1.58   | 1.84             | 1.60              |
| 5              | 60              | 1.35                         | 1.41                        | 1.52                            | -  | -                | -                 |
| 8              | 31              | 1.29                         | 0.95                        | 1.96                            | -  | -                | -                 |
| 10             | 25              | 1.28                         | 0.78                        | 2.06                            | 4.09   | 5.56             | 4.97              |
| 20             | 16              | 1.23                         | 0.42                        | 1.67                            | -  | -                | -                 |

**Table S3.** Viscosity ( $\eta$ ), density ( $\rho$ ), LiTFSA concentration ( $c$ ), ionic conductivity ( $\sigma$ ), and diffusivity ( $D$ ) of the LiTFSA–DMS electrolytes at 30 °C.

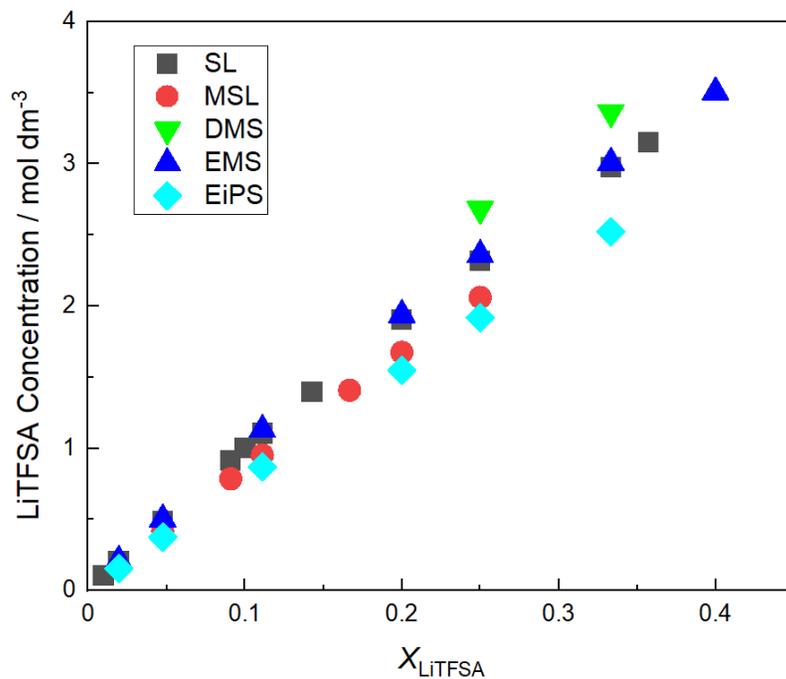
| [DMS]/[LiTFSA] | $\eta$<br>mPa s | $\rho$<br>g cm <sup>-3</sup> | $c$<br>mol dm <sup>-3</sup> | $\sigma$<br>mS cm <sup>-1</sup> | $D_{\text{Li}}$                                  | $D_{\text{sol}}$ | $D_{\text{TFSA}}$ |
|----------------|-----------------|------------------------------|-----------------------------|---------------------------------|--|------------------|-------------------|
|                |                 |                              |                             |                                 | 10 <sup>-7</sup> cm <sup>2</sup> s <sup>-1</sup> |                  |                   |
| 2              | 861             | 1.60                         | 3.36                        | 0.34                            | 0.26   | 0.27             | 0.19              |
| 3              | 206             | 1.53                         | 2.68                        | 0.98                            | 0.83   | 1.00             | 0.67              |

**Table S4.** Viscosity ( $\eta$ ), density ( $\rho$ ), LiTFSA concentration ( $c$ ), ionic conductivity ( $\sigma$ ), and diffusivity ( $D$ ) of the LiTFSA–EMS electrolytes at 30 °C.

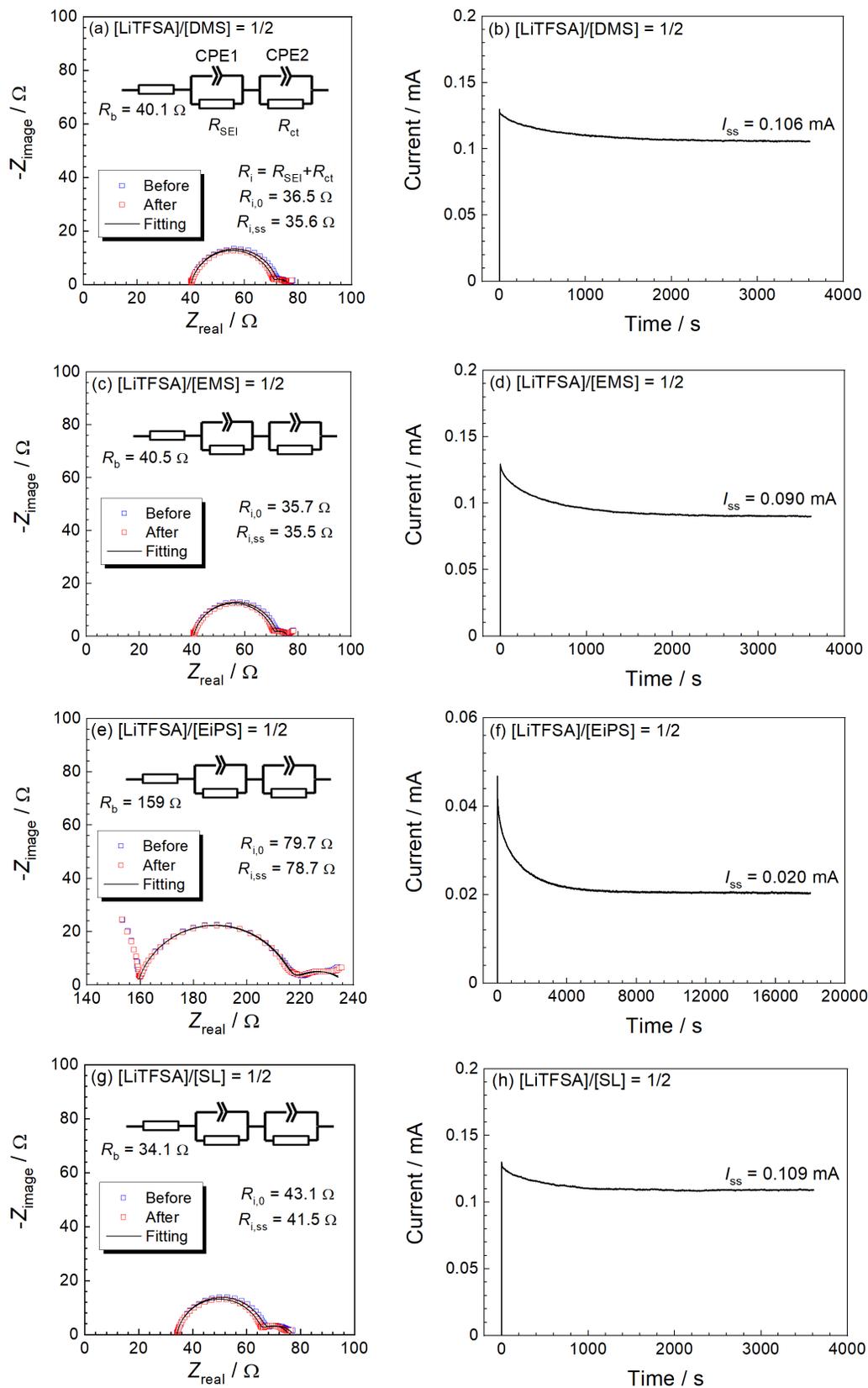
| [EMS]/[LiTFSA] | $\eta$<br>mPa s | $\rho$<br>g cm <sup>-3</sup> | $c$<br>mol dm <sup>-3</sup> | $\sigma$<br>mS cm <sup>-1</sup> | $D_{\text{Li}}$                                  | $D_{\text{sol}}$ | $D_{\text{TFSA}}$ |
|----------------|-----------------|------------------------------|-----------------------------|---------------------------------|--|------------------|-------------------|
|                |                 |                              |                             |                                 | 10 <sup>-7</sup> cm <sup>2</sup> s <sup>-1</sup> |                  |                   |
| 1.5            | 2205            | 1.57                         | 3.50                        | 0.13                            | -  | -                | -                 |
| 2              | 592             | 1.52                         | 3.01                        | 0.34                            | 0.24   | 0.30             | 0.21              |
| 3              | 159             | 1.44                         | 2.36                        | 0.91                            | 0.71   | 0.98             | 0.73              |
| 4              | 76              | 1.40                         | 1.94                        | 1.52                            | 1.31   | 2.06             | 1.57              |
| 8              | 22              | 1.30                         | 1.13                        | 2.67                            | 3.72   | 6.89             | 5.35              |
| 20             | 11              | 1.23                         | 0.50                        | 2.47                            | -  | -                | -                 |
| 50             | 8               | 1.19                         | 0.21                        | 1.41                            | -  | -                | -                 |

**Table S5.** Viscosity ( $\eta$ ), density ( $\rho$ ), LiTFSA concentration ( $c$ ), ionic conductivity ( $\sigma$ ), and diffusivity ( $D$ ) of the LiTFSA–EiPS electrolytes at 30 °C.

| [EiPS]/[LiTFSA] | $\eta$<br>mPa s | $\rho$<br>g cm <sup>-3</sup> | $c$<br>mol dm <sup>-3</sup> | $\sigma$<br>mS cm <sup>-1</sup> | $D_{\text{Li}}$                                  | $D_{\text{sol}}$ | $D_{\text{TFSA}}$ |
|-----------------|-----------------|------------------------------|-----------------------------|---------------------------------|--|------------------|-------------------|
|                 |                 |                              |                             |                                 | 10 <sup>-7</sup> cm <sup>2</sup> s <sup>-1</sup> |                  |                   |
| 2               | 1409            | 1.41                         | 2.52                        | 0.10                            | 0.08   | 0.11             | 0.10              |
| 3               | 281             | 1.33                         | 1.92                        | 0.31                            | 0.37   | 0.56             | 0.51              |
| 4               | 107             | 1.29                         | 1.55                        | 0.64                            | -  | -                | -                 |
| 8               | 22              | 1.20                         | 0.87                        | 1.76                            | 2.93   | 6.15             | 5.26              |
| 20              | 9               | 1.13                         | 0.38                        | 1.97                            | -  | -                | -                 |
| 50              | 6               | 1.10                         | 0.15                        | 1.21                            | -  | -                | -                 |



**Figure S2.** LiTFSA concentration (mol dm<sup>-3</sup>) as a function of the LiTFSA mole fraction ( $X_{\text{LiTFSA}}$ ) in LiTFSA/sulfone solutions at 30 °C.



**Figure S3.** (a, c, e, g) Nyquist plots and (b, d, f, h) chronoamperograms of symmetric Li/Li cells with electrolytes: (a, b) [LiTFSA]/[DMS]=1/2, (c, d) [LiTFSA]/[EMS]=1/2, (e, f) [LiTFSA]/[EiPS]=1/2, and (g, h) [LiTFSA]/[SL]=1/2. Chronoamperometry was performed at a constant voltage of 10 mV at 30 °C. Nyquist plots were obtained before and after chronoamperometry.

**Table S6.** Resistances in Li/Li symmetric cells evaluated by AC impedance and steady-state current observed by chronoamperometry of Li/Li symmetric cells (**Fig. S3**) for the determination of  $t_{\text{Li}}^{\text{abc}}$  in [LiTFSA]/[sulfone] = 1/2 electrolytes.

| sulfone | $R_b$ ( $\Omega$ ) | $R_{i,0}$ ( $\Omega$ ) | $R_{i,ss}$ ( $\Omega$ ) | $I_{\text{ohm}}$ (mA) | $I_{ss}$ (mA) | $\Delta V$ (mV) |
|---------|--------------------|------------------------|-------------------------|-----------------------|---------------|-----------------|
| SL      | 34.1               | 43.1                   | 41.5                    | 0.127                 | 0.109         | 9.83            |
| DMS     | 40.1               | 36.5                   | 35.6                    | 0.130                 | 0.106         | 9.97            |
| EMS     | 40.5               | 35.7                   | 35.5                    | 0.132                 | 0.090         | 10.05           |
| EiPS    | 159                | 79.7                   | 78.7                    | 0.043                 | 0.020         | 10.21           |