Liquid Range of Binary Solvents of Common Carbonates for Lithium Batteries

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The purpose of this presentation is to delineate the liquid range of binary solvents made of these five common carbonates: EC, PC, DMC, EMC, and DEC, and to observe and to discuss the importance of the change of the liquid range with the property of the end-members.[1,2]

Research and development in the area of lithium batteries has long established a number of organic carbonates as the most suitable solvents for making the nonaqueous electrolytes. This suitability comes firstly as a result of their wide electrochemical stability window, of which the low reduction limit enables lithium reduction and the high oxidation limit enables the use of some highly energetic oxides as the cathodes. It is secondly a result of the good physical properties of mixed carbonate solvents and the ease with which these properties can be tailored to particular applications by adjusting the proportions of the components. Typically, high dissolving power for lithium salts and high values of viscosity and dielectric constant are associated with the cyclic carbonates, and the noncyclic carbonates exhibit low values for these properties. Fortunately, when a cyclic carbonate is mixed with a noncyclic, the properties of the binary system change monotonically with the solvent composition.[3] This makes it relatively easy to optimize the properties of an electrolyte of a binary carbonate by altering the solvent composition. As a result, binary carbonates composed of a cyclic and a noncyclic carbonate have been the base solvents for many popular electrolytes in lithium batteries.

In addition to the above properties, stable liquid range of a solvent is another critical property for its proper use in lithium battery electrolytes, especially for low temperature applications.[4] But unlike the other properties, melting temperature of a binary solvent is usually lower than those of the components but changes with the solvent composition with little regularity. Therefore, liquid range of a binary solvent is usually empirically learned and graphically represented in the form of a liquid-solid binary phase diagram. Because of the popularity of the binary carbonates and the lack of information on their liquid ranges, we mapped with a differential scanning calorimeter the liquid-solid phase diagrams for all the binary combinations of these five common carbonates: EC, PC, DMC, EMC, and DEC. The results showed that all the carbonates formed simple eutectic binary systems, although their specific features varied greatly. DEC melted at –74.3 °C instead of the widely accepted value of –43 °C. Furthermore, the degree of expansion of the liquid range toward low temperature was primarily determined by compatibility in structure and closeness in melting temperature of the two components. The degree of expansion was highest when the two components were either both cyclic or both noncyclic (Fig. 1 and 2). For a cyclic-noncyclic combination, the degree increased with closer melting temperatures for the two components (Fig. 2). The last observation indicated that an expansion toward low temperature of a binary system was facilitated not by arbitrarily replacing one component with a lower-melting one but by having two components with close melting temperatures and similar molecular structures.

1. M. S. Ding, K. Xu, and T. R. Jow, *J. Electrochem. Soc.*, **147**, 1688 (2000)
2. M. S. Ding, K. Xu, S. S. Zhang, and T. R. Jow, *J. Electrochem. Soc.*, **148**, Issue 4 (2001)
3. G. E. Blomgren, in *Lithium Batteries*, J.-P. Gabano, Editor, p. 18, Academic Press, Ltd., London (1983)
4. S. P. Ding, K. Xu, S. S. Zhang, T. R. Jow, K. Amine, and G. L. Henriksen, *J. Electrochem. Soc.*, **146**, 3974 (1999)

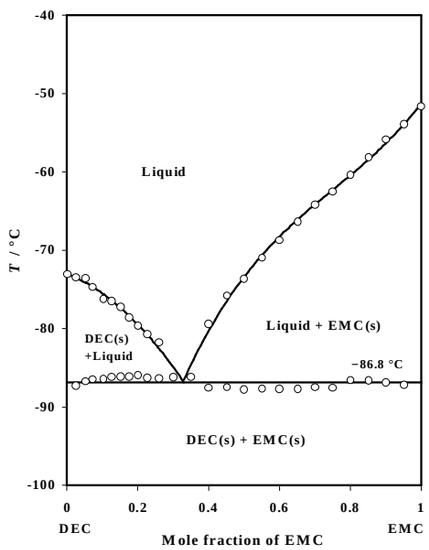

Figure 1. Liquid-solid phase diagram of DEC-EMC. The open dots represent measured data from which the curves and the line have been obtained through data fitting.

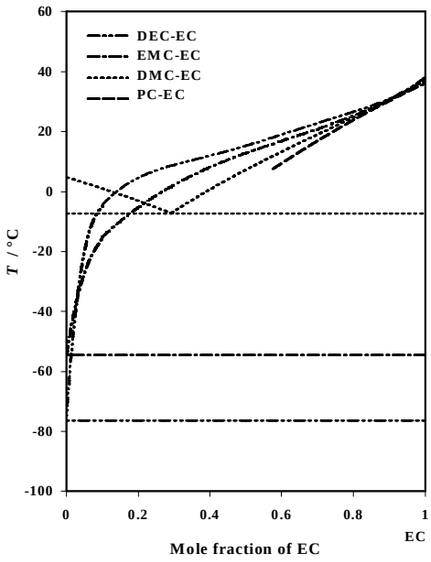

Figure 2. Liquid-solid phase diagrams of DEC-EC, EMC-EC, DMC-EC, and PC-EC combined with EC as the common component.