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Solvate Structures and Spectroscopic Characterization of $LiClO_4$ Electrolytes

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Current state-of-the-art electrolytes—mixtures of carbonate-based solvents with $LiPF_6$—are not stable at high voltages, especially at elevated temperature, so the development of new electrolyte solvents and salts are required for the progression of Li-ion battery technology (1). Many electrolyte mixtures have been introduced and tested for Li-ion batteries. Most of this work, however, has been done by a trial-and-error Edisonian approach (2). In part, this is due to the current limited understanding regarding electrolyte interactions at the molecular-level, specifically ionic association and Li^+ cation solvation. The properties of electrolytes are dictated by these molecular interactions, which are influenced by several factors, such as the structure of the anion and solvent, temperature and salt concentration. A greatly improved understanding of these properties will enable the rational design of electrolytes for a wide variety of battery chemistries and applications.

Raman vibrational spectroscopic analysis has been widely used to examine the solvent and anion interactions in both solid-state and liquid phases (3,4). Raman analysis is only a useful tool, however, if the assignment of the vibrational bands can be correctly linked with specific electrolyte interactions. It has been shown that solvate single crystals enable such assignments (5). In this study, a wide range of single crystal structures of $LiClO_4$ solvates have been used as model compounds for the assignment of Raman vibrational bands for specific forms of ClO_4^-...Li^+ cation coordination. The structures of the crystalline solvates have been obtained by single crystal X-ray diffraction analyses to determine the solvent and ion coordination within the crystalline solvates formed. The temperature dependence of the Raman bands, as shown in Figure 1, has been determined to further facilitate the deconvolution of the overlapping anion bands found in electrolyte solutions (i.e., the data from the known solids is used as a model for liquids). This information provides a crucial tool for the identification and characterization of the ionic association interactions within liquid electrolytes.

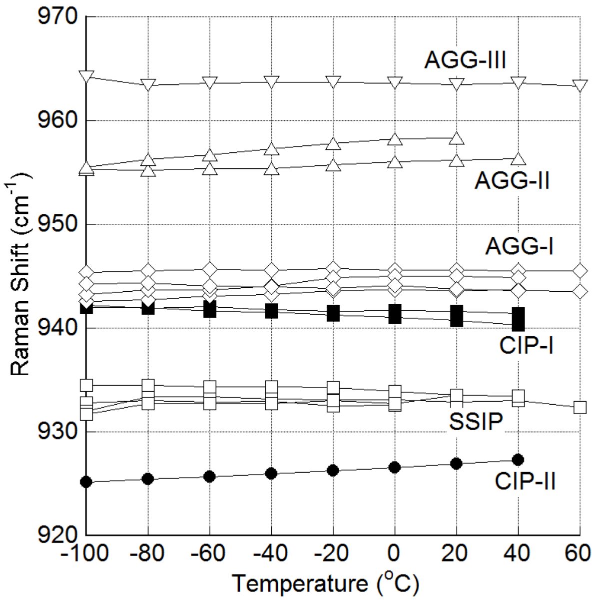

Figure 1. ClO_4^- anion Raman vibrational band peak position for crystalline solvates with various forms of ClO_4^-...Li^+ cation coordination.

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REFERENCES

1. K. Xu, *Chem. Rev.*, **104**, 4303 (2004).
2. J. T. Dudley, D. P. Wilkinson, G. Thomas, R. LeVae, S. Woo, H. Blom, C. Horvath, M. W. Juzkow, B. Denis, P. Juric, P. Aghakian, and J. R. Dahn, *J. Power Sources*, **35**, 59 (1991).
3. D. W. James, and R. E. Mayes, *Aust. J. Chem.*, **35**, 1775 (1982).
4. J. Grondin, D. Talaga, J.-C. Lasségues, and W. A. Henderson, *Phys. Chem. Chem. Phys.*, **6**, 938 (2004).
5. S.-D. Han, J. L. Allen, E. Jónsson, P. Johansson, D. W. McOwen, P. D. Boyle, and W. A. Henderson, *J. Phys. Chem. C*, **117**, 5521 (2013).