Spin Delocalization in Transition Metal Ion Complexes with Degraded Electrolyte Ligands Extracted from Li-ion Batteries

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Short Abstract

Upon operation of a Li-ion battery, transition metal ions from the cathode are dissolved into the electrolyte with a characteristic oxidation state and ligand shell. Investigation of dissolved vanadyl ions from vanadium oxide cathodes reveal fluorophosphoric acid derivatives to be the dominant ligands. Conformational flexibility and a highly structure-dependent spin delocalization mechanism results in an very large distribution of hyperfine coupling constants, which can be modelled by using a conformer distribution.

Long Abstract

Li-ion batteries are a key technology for the transition toward a sustainable transportation sector. Successful battery chemistries require a high Faradaic efficiency and long-term stability, which are particularly affected by chemical side-reactions, commonly involving degradation of the electrodes and electrolyte. First, transition metal ions in the electrolyte stemming from electrode dissolution need to be characterized regarding oxidation state and complexation to predict their behaviour in solution. Secondly, reactive trace species formed by electrolyte decomposition need to be identified to develop deactivation strategies.

As representative examples, vanadyl ions (VO^{2+}) dissolved from vanadium(+V) oxide cathodes are investigated.[1,2] The ligand sphere is determined via EPR hyperfine spectroscopy and compared with DFT and molecular dynamics calculations. The ligand identity depends on the operation and storage conditions. When stored at elevated temperatures, which enhances decomposition of the electrolyte salt $LiPF_6$, a complex is formed that shows a pronounced distribution of ^{31}P and ^{19}F hyperfine coupling constants. A large range of around 30 MHz for the coupling to ^{31}P is manifested in broad 'boomerang'-type[3] ridges in the HYSCORE spectrum. Bond and dihedral angles towards phosphoroxy ligands are identified to majorly influence the hyperfine coupling via spin delocalization. Similar ligand identities are obtained for Mn(II) ions, which are regarded most detrimental in Li-ion batteries,[4] hinting at the selectivity of the coordination by electrolyte degradation products.

[1] C. Szczuka, P. Jakes, R.-A. Eichel, J. Granwehr, *Adv. Energy Sustain. Res.* **2021**, *2*, 2100121.

[2] C. Szczuka, R.-A. Eichel, J. Granwehr, *ACS Appl. Energy Mater.* **2022**, *5*, 449–460.

[3] N.-A. Stamos, E. Ferentinos, M. Chrysina, C. P. Raptopoulou, V. Psycharis, Y. Sanakis, D. A. Pantazis, P. Kyritsis, G. Mitrikas, *Inorg. Chem.* **2020**, *59*, 3666–3676.

[4] R. Jung, F. Linsenmann, R. Thomas, J. Wandt, S. Solchenbach, F. Maglia, C. Stinner, M. Tromp, H. A. Gasteiger, *J. Electrochem. Soc.* **2019**, *166*, A378–A389.

ToC graphic

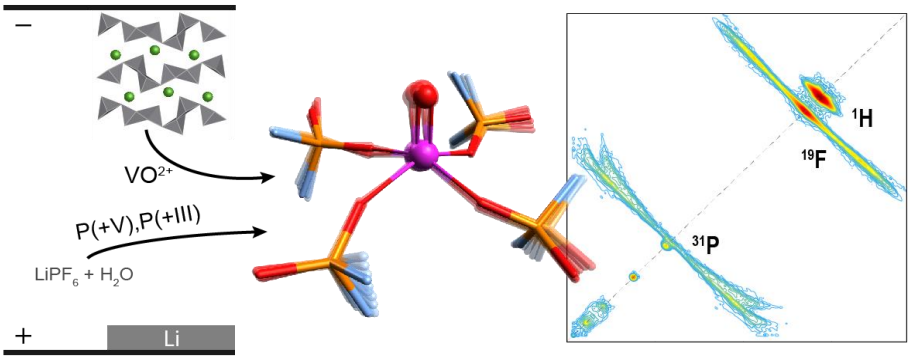

Figure 1: Schematic depiction of the formation of vanadyl ions with ligands originating from electrolyte degradation. Structural flexibility is manifested in HYSCORE traces.