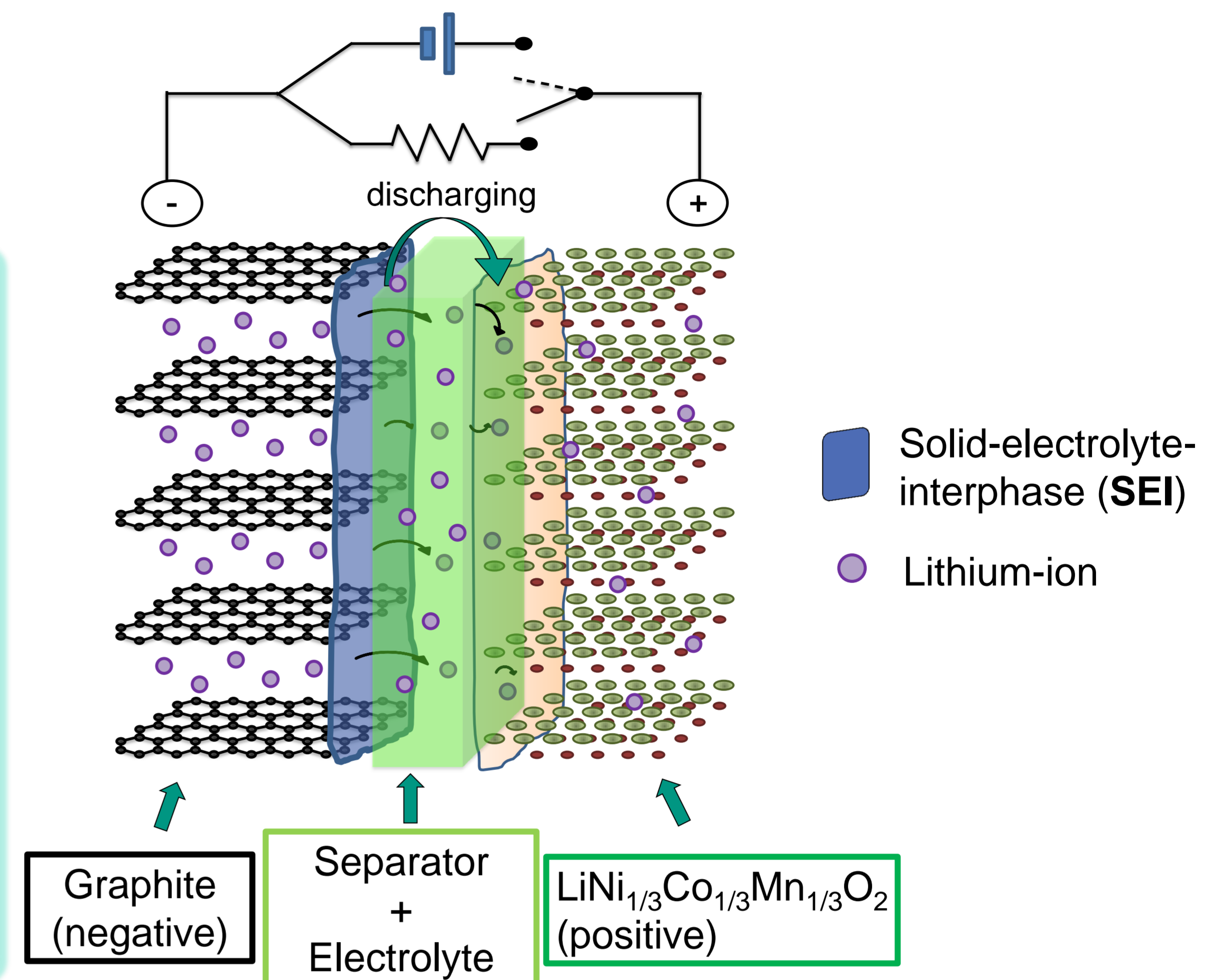


XPS characterization of graphite electrode interphases in lithium ion batteries

V. Winkler^{1,*}, M. Schulz¹, T. Hanemann^{1,2} and M. Bruns^{1,3}

Introduction

Due its high energy density lithium-ion batteries are very attractive for applications in hybrid or electric vehicles. In this new application field the cycle or shelf lifetime is of greater importance than in consumer electronics. It is well known that the formation of a stable interphase layer (SEI) on the anode side in state-of-the-art cells with graphite anodes plays a key role in this aging issue. This passivation layer is buildup of different electrolyte decomposition products. It effectively protects the electrolyte from a continuous decomposition or loss of active lithium and prevents the anode from destructive processes. This layer is only in the magnitude of a few tenths of nanometers. Therefore surface sensitive characterization methods like X-ray photoelectron spectroscopy (XPS) are needed to adequately analyze their properties. In this work different parameters like cycling characteristics and electrolyte composition were systematically studied to investigate various influences on the interphase formation and their respective composition.

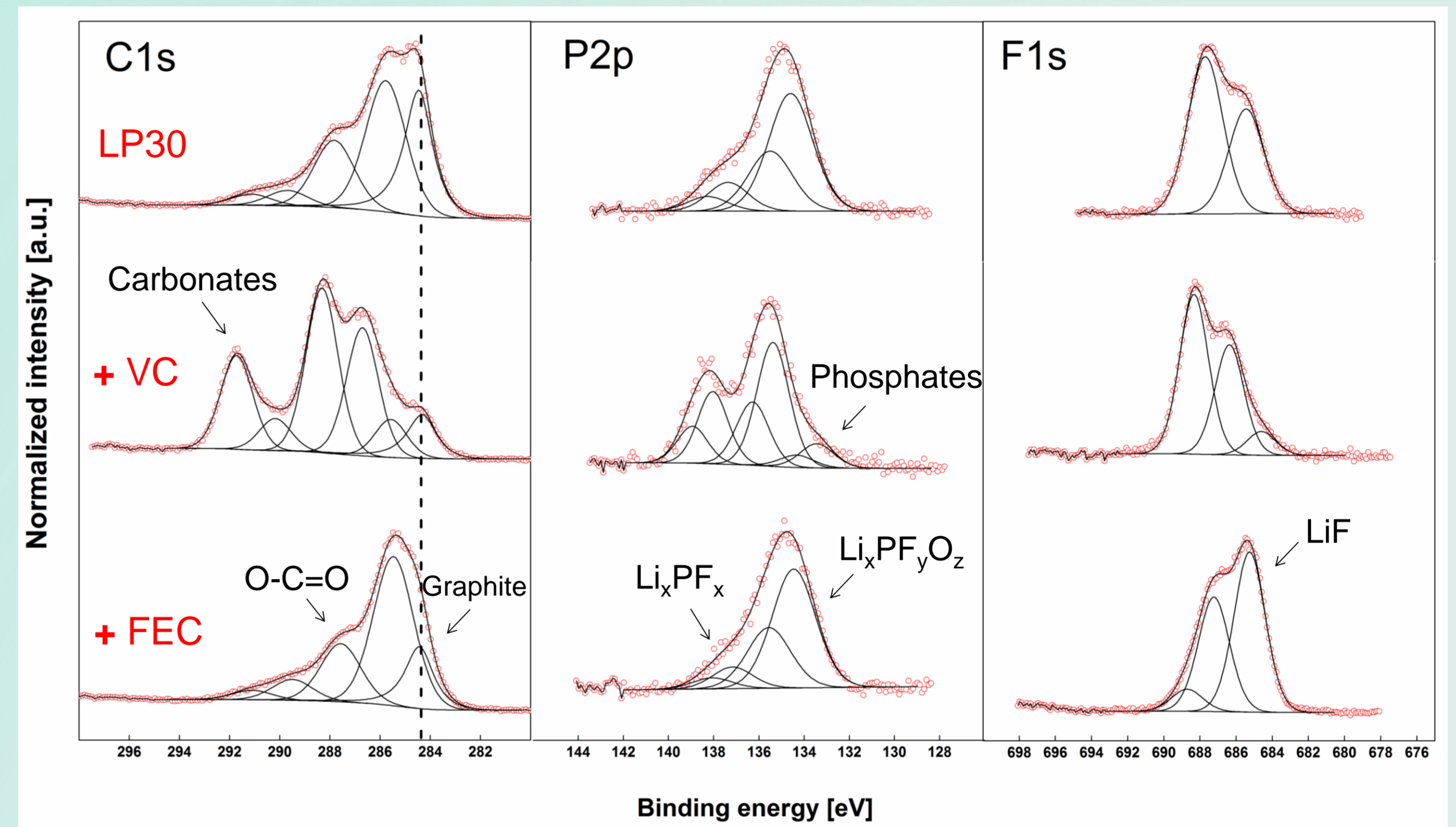


Slow cycling of the cell (C25 at RT)

Electrolytes based on organic carbonates (LP30) and different additives were used

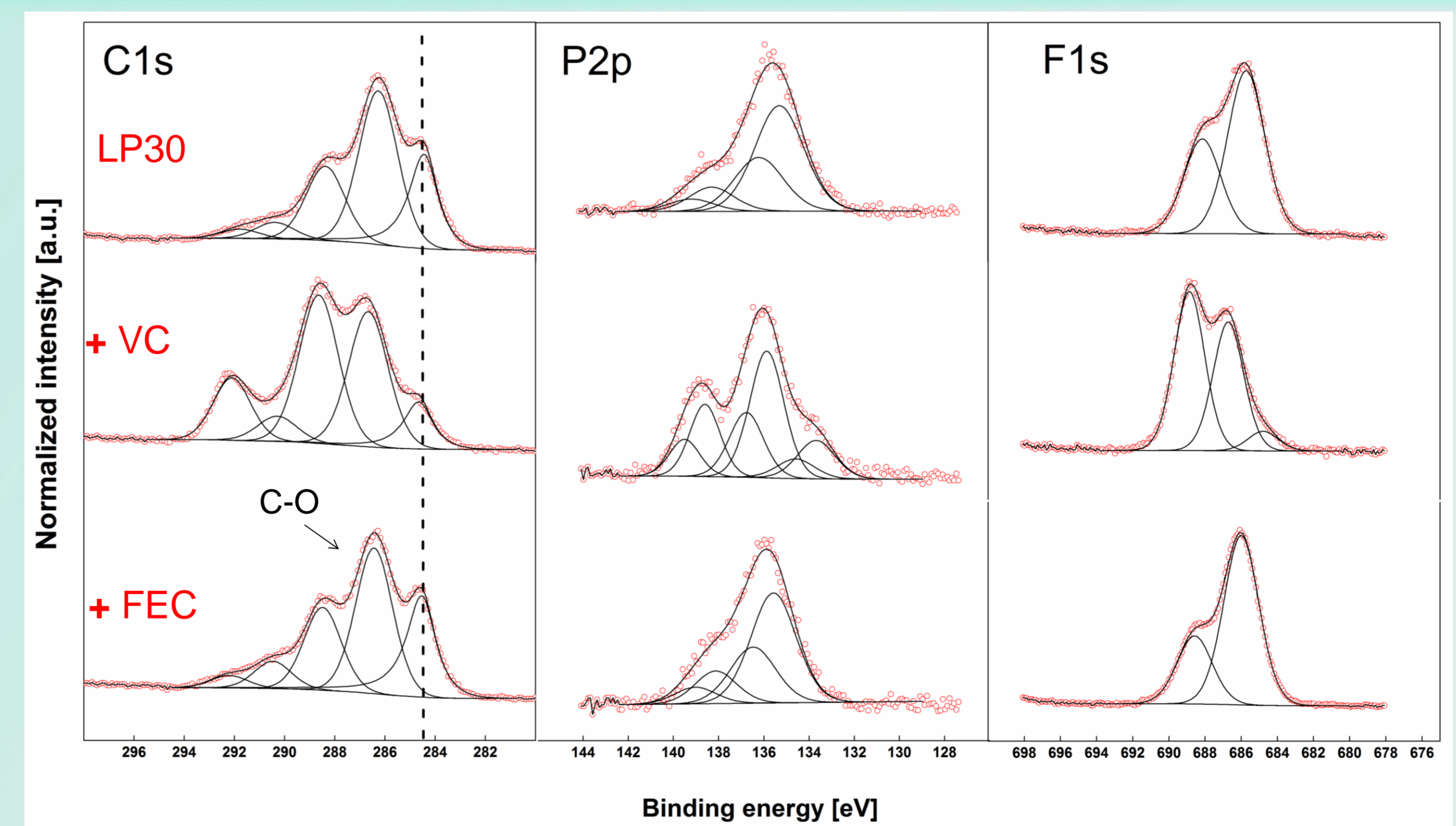
- VC (1,3-Dioxol-2-one) influences the mechanisms of conductive salt decomposition
- VC additive was built-in the SEI layer verified by higher carbonate quantity
- Carbonaceous species of LP30 and FEC (4-Fluoro-1,3-dioxolan-2-one) containing electrolyte are quite similar except the graphite peak relation
- FEC causes increasing of fluorine leading to formation of Lithiumfluoride (LiF)

* C/n: current rate when the cell is charged or discharged completely in n h



Faster cycling of the cell (C5 at RT)

- For VC containing electrolyte the charge-/discharge rate does not influence XP spectra of graphite
- Comparable fast decomposition kinetics of VC related reactions
- XP spectra of LP30 and FEC electrolyte were nearly identical
- Pronounced hydroxy-/ether carbon species
- Fluorine release of FEC is significantly reduced compared to C25, although Lithiumfluoride is still the leading fluorine species
- Other reaction pathways are preferred over FEC involved decomposition reactions



Experimental

X-ray Photoelectron Spectroscopy (XPS):

ThermoFisher Scientific K-Alpha Spectrometer

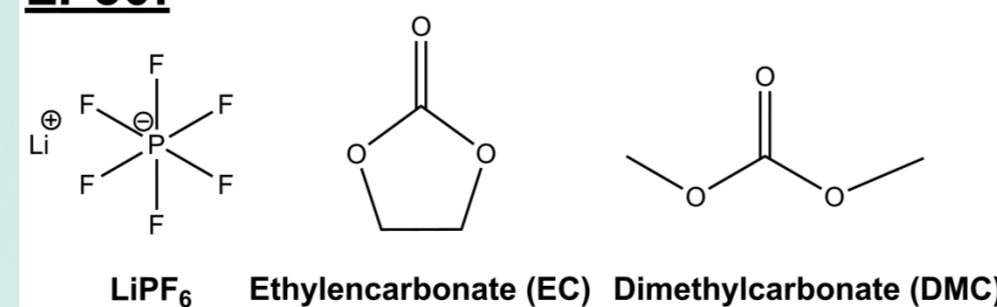
- Micro-focused mono-Al-K α X-ray source
- Charge compensation with low energy electrons and Ar⁺-Ions

Sample preparation:

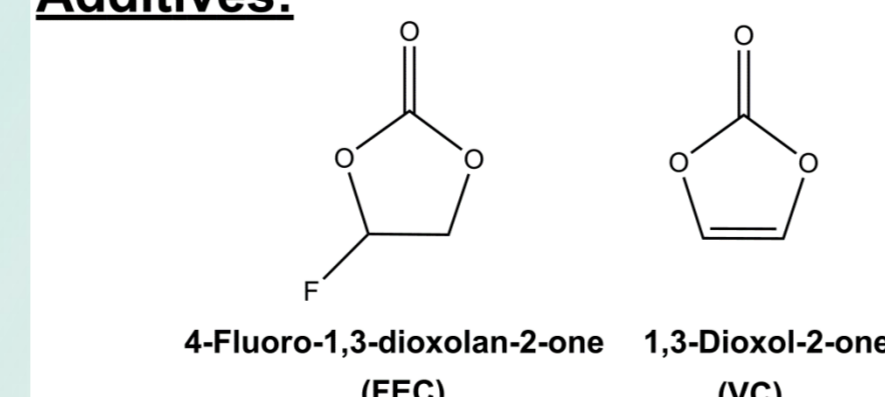
- Swagelok-type half-cells of graphite (vs. Li) were galvanostatically charged/discharged between 0-2V
- Samples were carefully rinsed prior to XPS analysis
- Sample handling and transportation under inert gas

Electrolyte components:

LP30:



Additives:



Conclusions

- Only small amounts (1-2%) of additives can change the SEI composition significantly
- Cell operation conditions influences the SEI composition
 - Battery performance is directly linked with SEI composition
 - Built-up of SEI layer is not only defined by electrolyte formation but also by operation conditions
- Different decomposition kinetics of electrolyte components changed the SEI composition
 - Electrolyte mixture should be carefully reviewed