Organic Electrode Materials for Lithium-Ion Batteries

Peter Bäuerle[1], Elena Mena-Osteritz[1], Pierre-Olivier Schwartz[1],
Djawed Nauroozi[1], Günther Götz[1]*, Marijana Pejic[2], and Mario Wachtler[2]**

[1]Institut für Organische Chemie II und Neue Materialien, Universität Ulm, Albert-Einstein-Allee 11, D-89081 Ulm

[2]ZSW – Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Helmholtzstr. 8, D-89081 Ulm

*☎+49-731-50/22841, e-mail: guenther.goetz@uni-ulm.de, **☎+49-731-9530-403, Fax +49-731-9530-666, e-mail: mario.wachtler@zsw-bw.de

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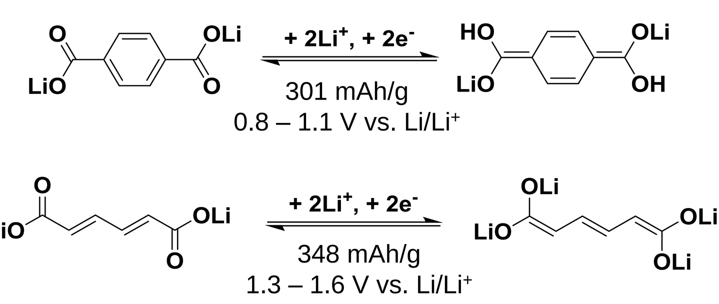
Introduction

Organic electrode materials have been proposed as metal-free alternatives to state-of-the-art inorganic LIB electrode materials, recently.[1,2,3]

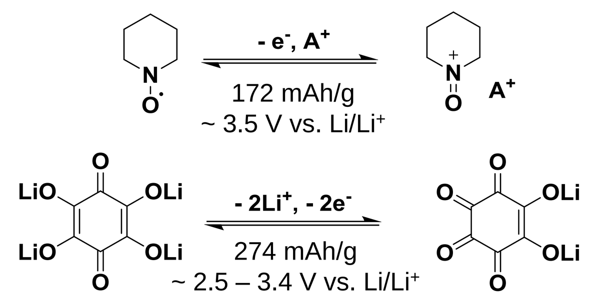
General concepts:

	ANODE	CATHODE
Li-ion type	$A + n\,Li^+ + n\,e^- \leftrightarrow Li_nA$	$Li_mC \leftrightarrow C + m\,Li^+ + m\,e^-$
Dual-ion type	$A + n\,Li^+ + n\,e^- \leftrightarrow Li_nA$	$C + m\,X^- \leftrightarrow CX_m + m\,e^-$

Typical anode materials



Typical cathode materials



Challenges:

- Reversibility of redox process and stability of reduced and oxidised forms of electrode material
- Electrode preparation (esp. solvent-based preparation with Li-containing anode materials)
- Solubility of organic materials in electrolyte, resulting in capacity fade and self-discharge (by redox-shuttle action)
- Synthesis / preparation of thick electrodes (in view of cells with high volumetric capacity)

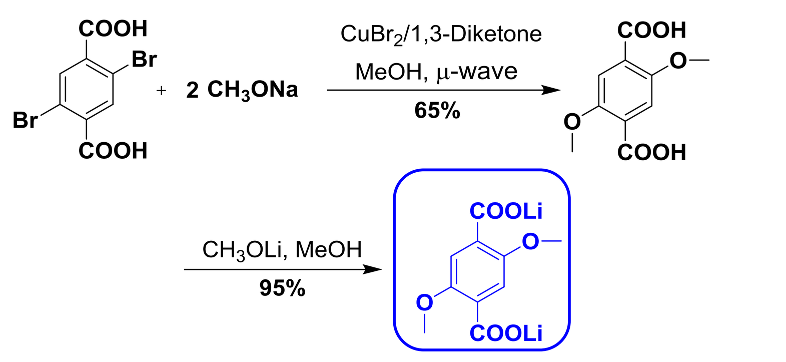
Strategies:

- Immobilisation of functional units on polymers
- Optimised and alternative electrode preparation methods
- Use of conductive polymers as electrode back-bone, binder, and conductive additive

Aim of the work

Development of an organic electrode couple with a practical capacity of >150 mAh/g and a cell voltage of >1.9 V (which would compare to a $Li_4Ti_5O_{12}$-$LiFePO_4$ Li-ion cell).

Organic building block as electrode material



Scheme 1: Synthesis of redox-active Li-carboxylate-substitued benzene[4] as anode material.

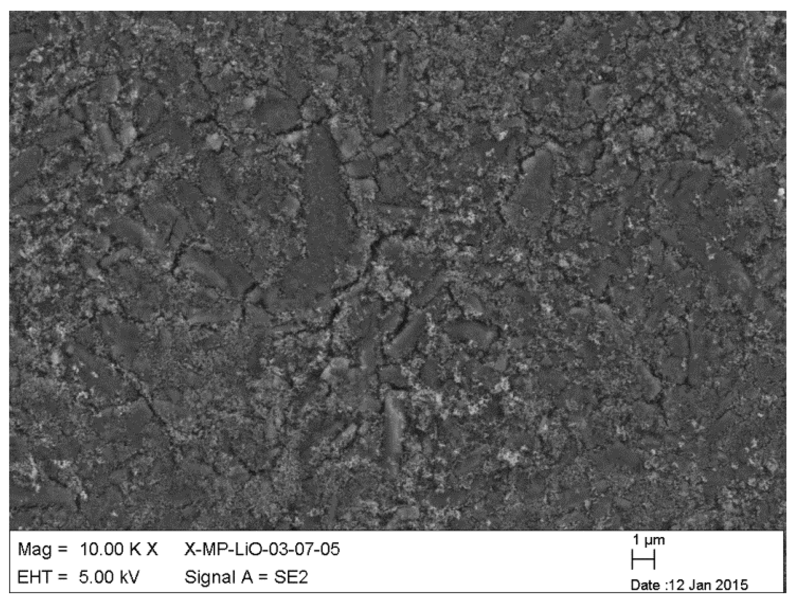


Figure 1: SEM investigation of the electrode prepared by solvent-free method.

Electrochemical performance

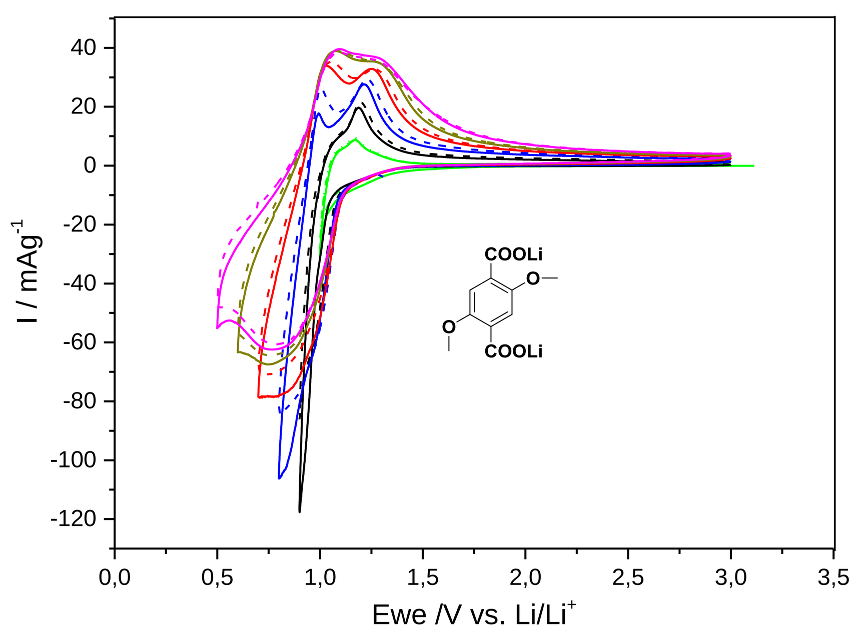


Figure 2: Cyclic voltammetry measurement of the redox-active Li-carboxylate-substitued benzene in solution (1 M $LiPF_6$ in EC:DMC (1:1 wt.), v_{scan} = 0.1 mV s[-1], 1... 0.5-3 V *vs* Li/Li+).

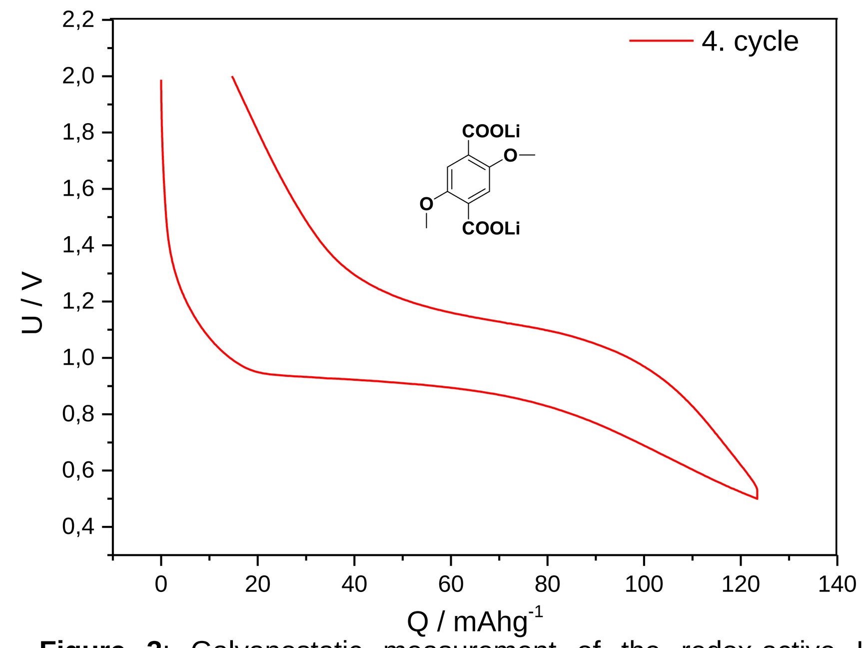
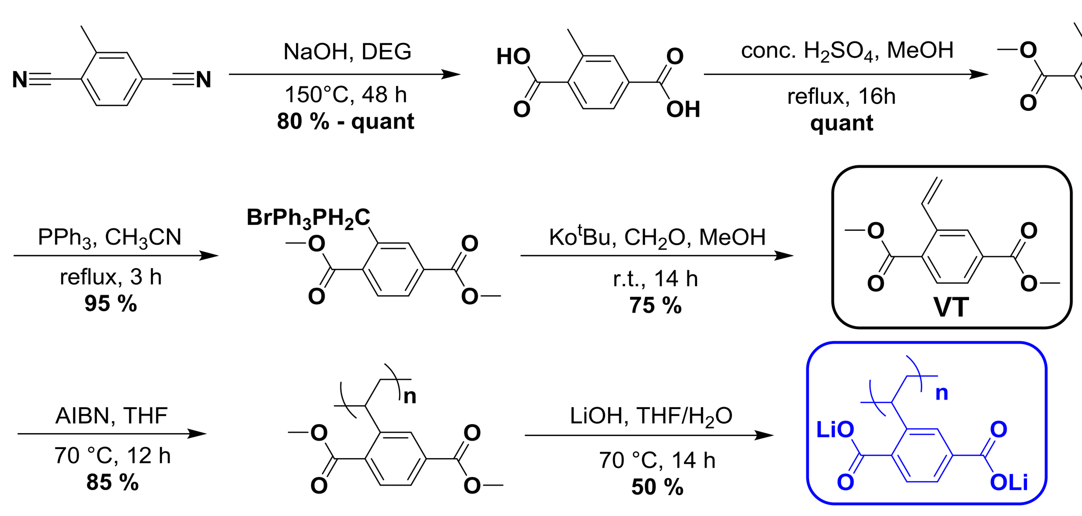


Figure 3: Galvanostatic measurement of the redox-active Li-carboxylate-substitued benzene (1 M $LiPF_6$ in EC:DMC (1:1 wt.), 4. cycle, v_{scan} = 0.1 mV s[-1], 0.5-2 V *vs* Li/Li+, C/10).

Redox-active polymers for anode



Scheme 2: Synthesis of lithiated terephthalate polymer by hydrolysis of the corresponding ester with LiOH. The vinyl terephthalate (VT) monomer was fashioned by a polymerisable vinyl unit and corboxylic esters for Li-insertion.

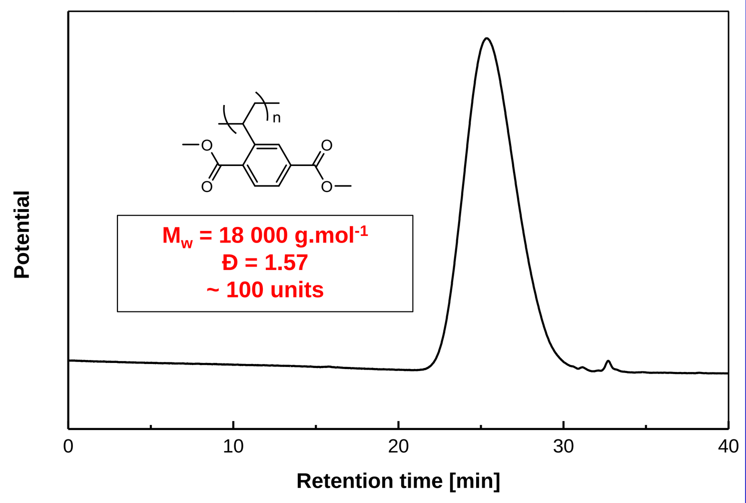
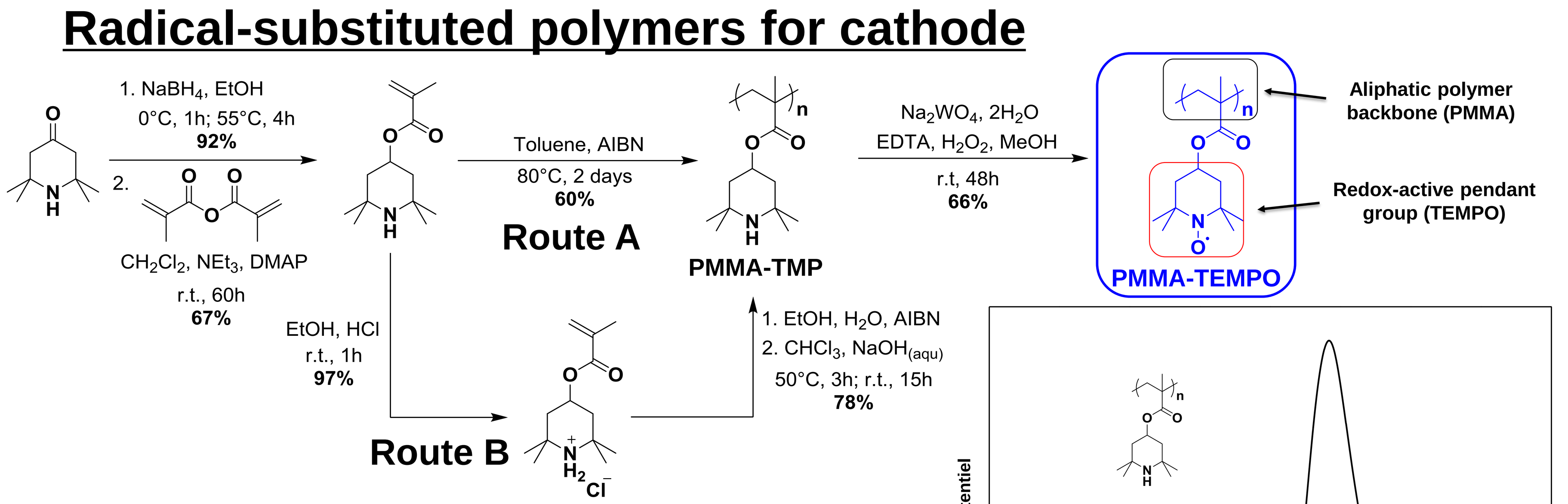


Figure 4: GPC-spectrum of the VT polymer and its characteristics.

Radical-substituted polymers for cathode



Scheme 3: Synthesis of polymethylmethacrylate-TEMPO (PMMA-TMP) by using two different polymerization routes: usual radical polymerization (Route A) and water-radical polymerization (Route B), followed by a N-Oxidation step.[5]

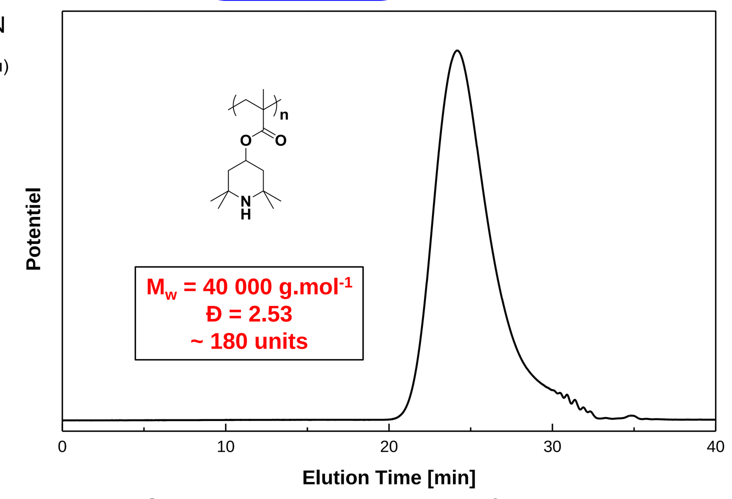


Figure 7: GPC-spectrum of PMMA-TMP and its characteristics

IR and CV Characterizations

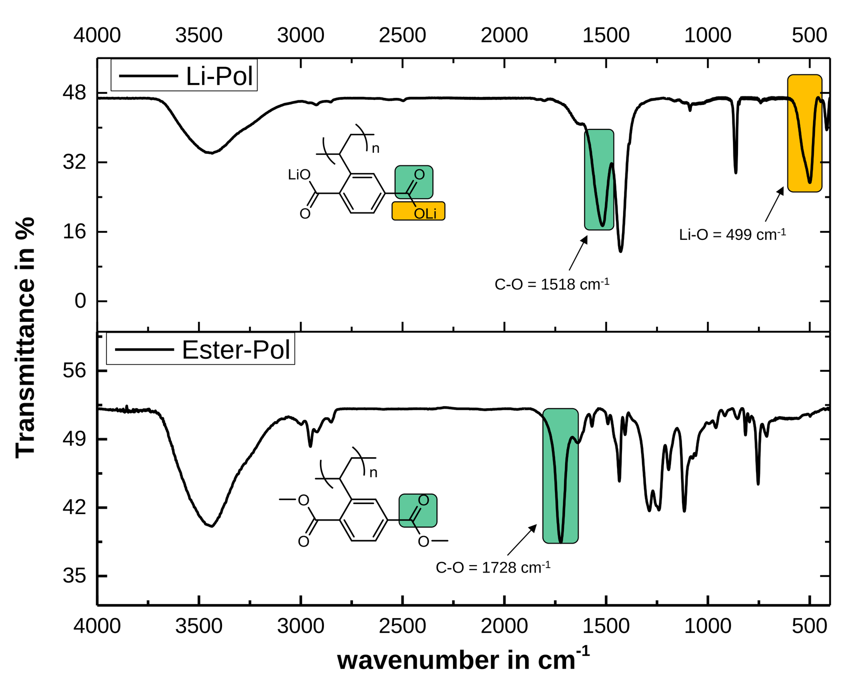


Figure 5: IR-spectra of the VT polymer and the lithiated counterpart. The characteristic Li-O band at *v* = 499 cm[-1] and the shift of the carbonyl band compared to the non-lithiated polymer are assigned, respectively.

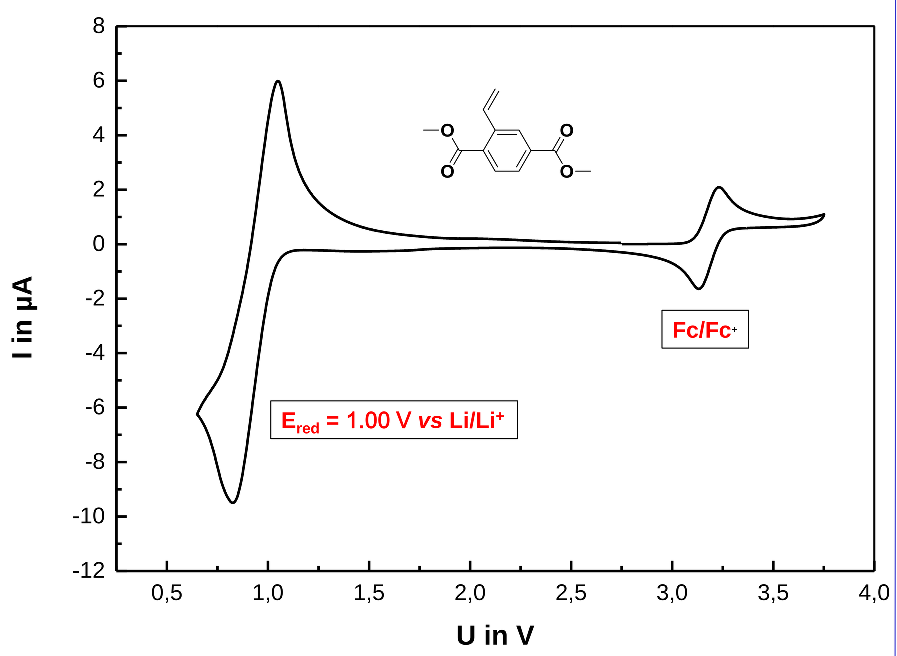


Figure 6: Cyclic voltammetry measurement of VT in solution (0.1 M solution of VT in THF, v_{scan} = 0.1 mV s[-1], $TBAPF_6$ as electrolyte, referenced against Li/Li+).

IR and CV Characterizations

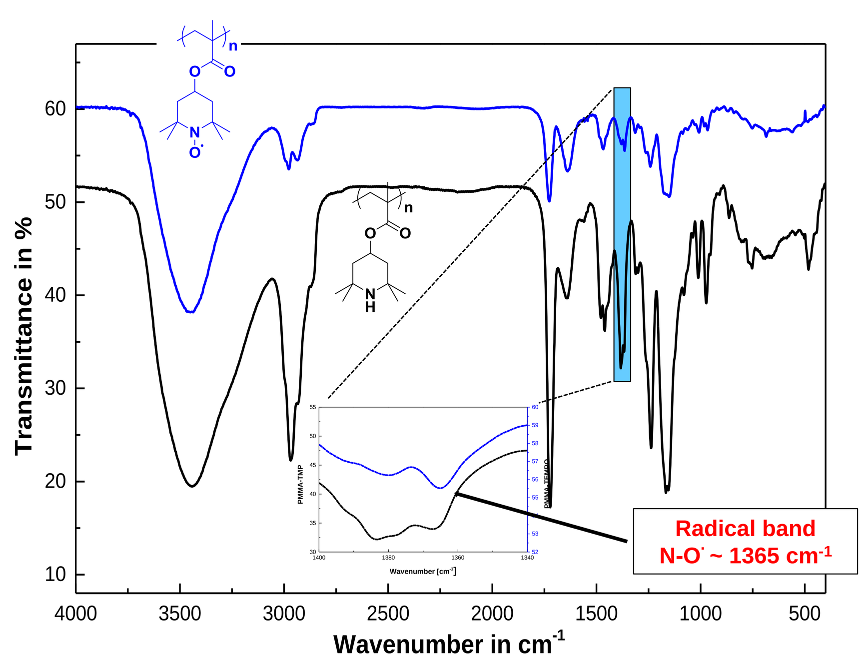


Figure 8: IR-spectra of PMMA-TMP (black) and PMMA-TEMPO (blue) polymers. The characteristic N-O· band at *v* = 1365 cm[-1] increases after N-oxidation of the PMMA-TMP.

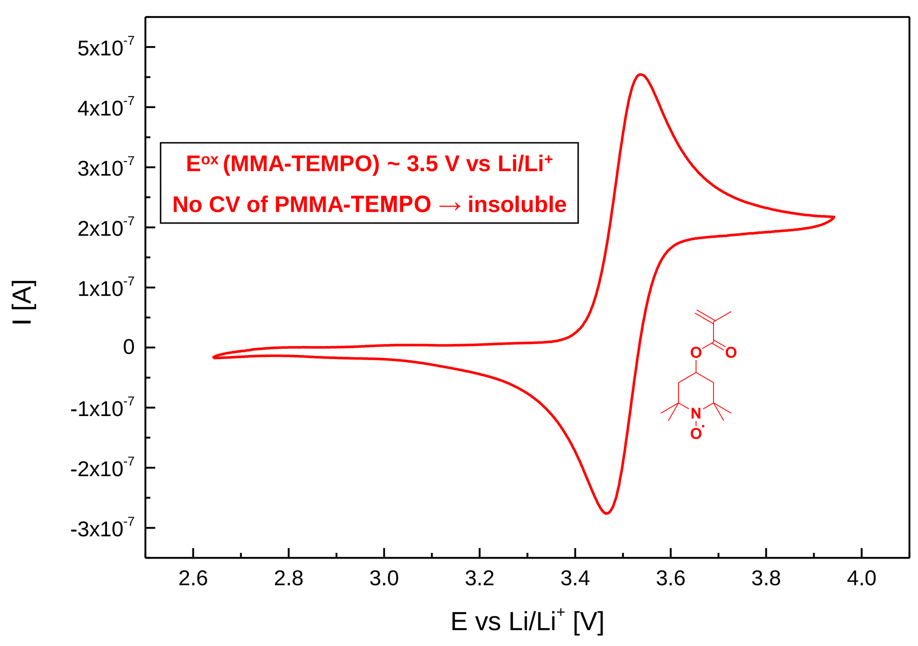


Figure 9: Cyclic voltammetry measurement of the monomer MMA-TEMPO (red) in solution (0.1 M in CH_3CN, v_{scan} = 0.1 mV s[-1], $TBAPF_6$ as electrolyte, referenced against Li/Li+).

Summary/Outlook

- In a first approach N-Oxyl radicals and arylic dicarboxylates are selected as organic materials for energy storage
- TEMPO- and Terephthalate moieties have been successfully immobilized on aliphatic polymer scaffold for application as cathode and anode materials
- Preparation of electrodes and their electrochemical properties are under investigation
- Possible application of conducting polymers in organic battery cells will be investigated

Acknowledgement

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