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# A Method to Measure the Swelling of Water-Soluble PVDF Binder System and Its Electrochemical Performance for Lithium Ion Batteries

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Water-soluble CMC/PVDF binder systems were used to prepare graphite anodes and compared mechanically and electrochemically with CMC/SBR binder systems. The effect of crystallinity of PVDF binder on the mechanical and electrochemical performance of the anodes is studied. A contact free method easy to operate and equipped with high accuracy was developed by using capacitance measurement. The swelling of graphite electrodes was controlled and showed different results for different binder crystallinities (no swelling of binder with high crystallinity vs 12% for medium crystallinity and 17% for low crystallinity binder). The discharge capacity depends on the crystallinity of the binders and half-cells delivered a capacity in the range of 230–360 mAh $g^{-1}$. The binder with medium crystallinity in particular exhibited the best mechanical and electrochemical performance and showed an excellent C-rate stability with specific capacities up to 10 C. Full cell tests showed good cycling stability over 180 cycles. The water-based PVDF binders seem to be a promising alternative to solvent-based binders.
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Lithium ion batteries (LIB) are still undergoing a development process regarding the energy density, power density, life time, safety and cost. Different types of active materials, binders and separators have been introduced in the LIB market. The aim of a binder is to adhere the active material particles and conducting additives together to form a continuous electric conduction path to the current collector.[1] Very often the binders influence on cell performance is underestimated, as they are considered as electrochemically inactive materials.[2] Commercial LIB are mostly using Polyvinylidene fluoride (PVDF) binder to fabricate the electrodes. The use of harmful and expensive organic solvents such as N-methy-2-pyrolidone (NMP) is required to dissolve the PVDF binder for preparation of the slurry.[3] To overcome these drawbacks especially concerning safety and because of ecological reasons, a novel fluorinated binder in aqueous dispersion has been introduced by Solvay Specialty Polymers, Italy, consisting of nano-sized (~250 nm) primary particles of PVDF in the shape of spheres.[4]

Mostly, PVDF aqueous dispersions are produced by a heterophase emulsion polymerization.[5] In addition, the particles are modified with polar monomers in order to increase the adhesion. Advantageously, no organic solvent is required to dissolve this PVDF dispersion. Lithium Cobalt Oxide electrodes have already been prepared in aqueous PVDF-binder.[6]

The present work introduces PVDF binder based aqueous electrode fabrication process for preparing the graphite electrodes. The study includes a peeling test, swelling test and electrochemical tests in half-cell and full cell configurations. Normally, the crystallinity of the binder influences the performance of a cell due to swelling occurring by the carbonate based electrolytes.[7] Therefore, the effect of crystallinity on the physical swelling of anode electrodes is investigated. A volumetric evolution of polymers (binders, dispersive agents) after soaking in the electrolyte or the uptake of organic electrolyte due to electrolyte-binder interactions[8] is named as physical swelling. The electrode swelling due to lattice expansion during cycling is called electrochemical swelling and is a well-known and well-described phenomenon.[8]

The swelling behavior of separators as well as of graphite anode in Lithium Ion Batteries have already been investigated.[9–12] Usually, swelling behavior is tested by measuring thickness and mechanical properties in several solvent environments.[3,13] It has been reported that a polymer with high crystallinity shows high solvent resistance, as the crystalline domains are not swollen by a solvent. Scratch test showed that a higher crystallinity also leads to better adhesion strength.[8] Some research groups have reported the swelling behavior of polymeric binders or swelling within the composite electrode, as physical swelling needs to be investigated in a qualitative and quantitative way.[7,12] The swelling of PVDF polymers in a carbonate electrolyte has been measured by using quartz crystal microbalance.[7] Scanning electron microscopy has also used to measure the swelling of a PVDF polymer in an EC:DC electrolyte with 1 M $LiPF_6$ quantitatively but after applying the electrolyte, the system needs 30 min to measure the thickness of polymer.[12] Anode swelling has also been investigated by using a selective shielding cathode, where electrodes with high mechanical strength are required in order to stand against the stress during process.[8]

We will concentrate on the physical swelling and implement a measurement technology that can be used rapidly as well as during processing. This article also presents the swelling measurements on the anode electrodes that can be performed with low efforts, on-line and without the necessity of a controlled atmosphere at very high accuracy starting at that time when the first drop of the electrolyte is placed upon the anode surface. Furthermore, this method can also be used to get information about crystallinity.

## Experimental

***Electrode preparation.***—Commercially available battery grade anode material graphite (MAGD, Hitachi Chemical, Japan) and cathode material $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC-3102, BASF, Germany) were used as active materials. Conductive carbon (Super C65, Timcal, Belgium) and cathode conductive graphite (KS6L, Timcal, Belgium) were used as conductive additives. For cathode preparation, PVDF (Solef 5130, Solvay Specialty Polymers, Italy) was used as binder. For anode preparation, a mixture of CMC (MAC 200 HC, Nippon paper Industries) and SBR binder (ZEON BM451, ZEON, Japan) or PVDF binder (different degrees of crystallinity, Solvay Specialty Polymers, Italy) were used. The used emulsions are stored at room temperature and homogenized before usage. The binder crystallinity was determined by DSC and found out to be 12% (low crystallinity PVDF), 30% (medium crystallinity PVDF) and 40% (high crystallinity PVDF).

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N-methyl-pyrrolidone (Overlack, 99,8%) was used as a solvent for the cathode, whereas deionized water was used as a solvent for the anode. 1 M $LiPF_6$ in ethylene carbonate and vinylene carbonate (Selectilyte RD1001, BASF) was used as electrolyte. For half cells, a glass-fiber Separator (Sartorius) was used, whereas for preparation of full cells, an inorganic-filled PVDF-separator was used.

The cathode was prepared by mixing NMC (93%), PVDF (3%), Super C65 (3%) and KS6L graphite (1%) with NMP solvent to have a solid content of 60%. The anode was prepared by mixing graphite (95%), carbon black (1%), CMC binder (1.33%), SBR binder (2.67%) —respectively an amount of 2.67% of PVDF binder with different crystallinities—and SuperC65 carbon black with deionised water to have a solid content of 45%. The cathode was prepared in a planetary mixer (Thinky Mixer AR-250-C3), the anode in a high-speed dissolver (Dispermat CV3-plus, VMA-Getzmann GmbH). Viscosity of anode slurries was measured with a Brookfield DV3T viscometer and resulted in values between 7675 and 8038 mPa.s. The anode slurries were casted by a doctor-blade coater in a roll-to-roll process coating machine on a Cu-foil current collector and dried in-line in a two-step drying tunnel at a temperature range of 95 °C–115 °C. The average mass loading was 1.35–1.50 mAh $cm^{-12}$. A field emission scanning electron microscope (FE-SEM) (Merlin Compact, Zeiss, Germany) with energy dispersive X-ray spectroscopy (EDX) was used to take EDX element mapping images to check binder distribution. The charging and discharging procedures for half-cell measurements are performed in a three-electrode-arrangement in Swagelok® cells. Adjustment of voltage is done by a pseudo-reference electrode (RE) consisting of elementary Lithium. The counter electrode (CE) also consists of elementary Lithium, whereas as working electrode (WE) the anodes to be investigated are used. A schematic set-up can be found in supplementary data.

The anodes were cut into round pieces with a diameter of 12 mm and dried at 110 °C for 24 h under vacuum. The Swagelok setup was assembled in an argon filled glove box (MB20, $H_2O$ and $O_2 < 1$ ppm). For both reference and counter electrode, Lithium metal was used.

Full cell measurements were performed in pouch foil with active areas of anode and cathode of 5.4 × 8.4 $cm^2$ and 5.0 × 8.0 $cm^2$ respectively. All parts were laminated with the help of a laminator at a line force of 157 $N.cm^{-1}$ in a temperature range of 110 °C–120 °C. The stacks were then dried at 110 °C for 24 h under vacuum and then placed in an argon filled glovebox (MB20, $H_2O$ and $O_2 < 1$ ppm), where the electrolyte was filled in and the cell was sealed. The cell was tempered at 60 °C for 4 h before starting of the electrochemical characterization.

***Mechanical characterization.***—Peeling tests were performed by cutting specimens from each coating thickness with a size of 50 × 80 mm and stuck with a two-folded adhesive tape upon the supporting surface. A 19 mm adhesive tape was pressed upon the coating and then tried to peel it off with a Peel-off Force Special Test Stand (TPE 50, Sauter GmbH) orthogonal to the supporting surface. The resulting force is noted and the optical result described.

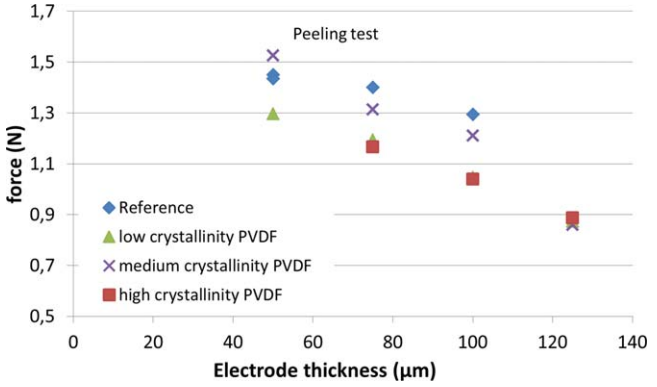


**Figure 1.** Results peeling test for different crystallinities and electrode thicknesses.

Bending tests were performed by bending the coated foil around a roll with a diameter of 1 cm. Adhesive or cohesive breaking is evaluator assessed.

To perform swelling tests, anodes were cut into pieces of 10 cm × 16 cm and placed on the measurement table. In order to prevent from solvent evaporation, the set-up was covered by PE foil and a syringe was placed through a small hole in the PE foil, so that solvent can directly drop on the coated electrode. The defined amount of solvent in a certain time span was controlled by a syringe pump. The capacitance sensor (capaNCDT SERIE 6100, Micro-Epsilon) was placed 1 cm next to the syringe to measure the change in coated thickness with time. For swelling test, electrolyte containing a mixture of ethylene carbonate and dimethylene carbonate in a weight ratio of 5:1 but without $LiPF_6$ conducting salt is used. These tests have been performed under normal atmosphere, so due to the danger of a decomposition of the conducting salt only a mixture of EC:DMC was used. The amount of electrolyte, 250 $\mu$l, was applied at a rate of 100 $\mu$l $min^{-1}$. Due to the set-up, we were only concentrating on the time shortly after solvent addition, as the set-up allows a redistribution as well as evaporation of the electrolyte. Here only the sudden soaking of electrolyte into the electrode framework is studied.

***Electrochemical characterization.***—The electrochemical characterization was performed with a battery tester (CTS-lab, BaSyTec), using galvanostatic (CC) and potentiostatic (CV) modes for charging and CC mode for discharging step. For half-cell measurements of the graphite anode, the voltage range was adjusted to 0.02–1.5 V and for full cell measurements, the voltage range was adjusted to 3.0–4.2 V. Formation was done for both half and full cells by two cycles of 0.1 C, which was calculated by the active material weight and theoretical capacities of NMC of 168 mAh · $g^{-1}$ and graphite of 372 mAh · $g^{-1}$.

Half-cell measurements were performed by combining the different anodes with elementary Lithium. For evaluation in Swagelok® three-electrode-cells, the anodes need to be cut in circular discs with a diameter of 12 mm (see figure A·1 in Appendix). Full cell tests were performed by combining the prepared anodes with NCM cathodes. To study the electrochemical performance of the anode without having any influence from cathode, the oversized cathode ∼30% is used in pouch cell format.

## Results and Discussion

***Mechanical tests.***—In order to measure quantitatively the adhesion strength of the electrode coating and cohesion of the particles throughout the coating, a peeling test is performed. The results of peeling test are shown in Fig. 1. The resulting forces are measured and adhesive (electrode coating partially delaminated) and/or cohesive (electrode coating damaged) breakings are observed.

As can be seen from Fig. 1, a reduction in the peeling force required to peel off the adhesive tape is observed upon increasing the thickness of the electrodes. Reference and medium crystallinity PVDF containing anodes required the highest peeling force in comparison to the other anodes in the thickness range from 50 $\mu$m to 100 $\mu$m, while all anodes showed similar peeling force at a thickness of 125 $\mu$m. A schematic drawing and the set-up of the bending test can be found in Figs. A·2 and A·3, Appendix.

Binder crystallinity also shows an effect on the mechanical strength.[9] It is reported that higher crystallinity exhibits higher scratch adhesion strength.[9] In contrast to this statement, the adhesion for medium crystallinity binder is found to be higher than for the one with high crystallinity. Because of the used latex form it has to be completely melted to reach best intrinsic adhesion. This is the case for the binder system with medium crystallinity while the highly crystalline binder system is reasonably not melted due to its higher melting point. Compared to the low crystallinity binder system, the

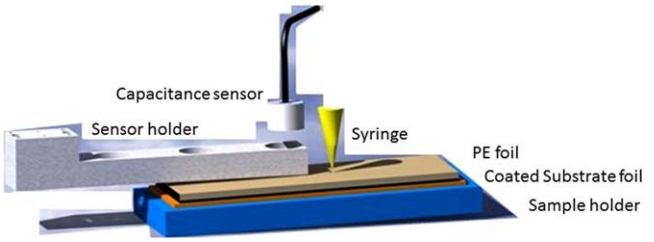


**Figure 2.** Schematic model of the capacitive displacement measurement method.

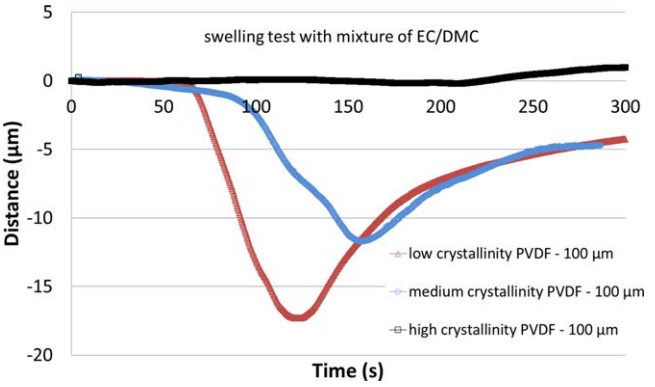


**Figure 3.** Swelling tests of binders with different crystallinities with mixture of EC/DMC.

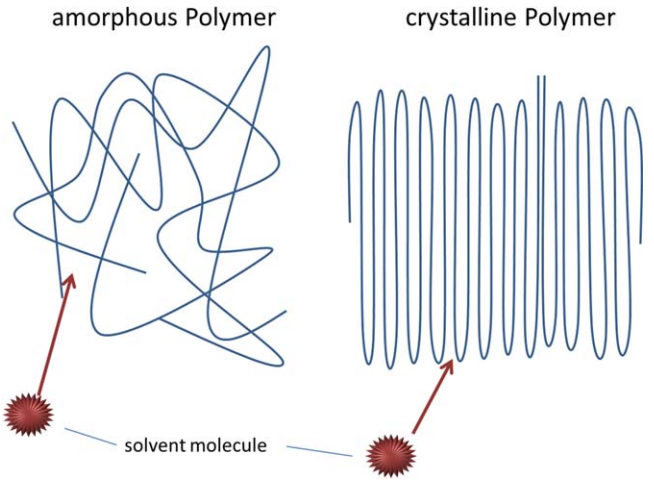


**Figure 4.** Solvent penetration of amorphous and crystalline polymer.

medium-crystalline system has higher intrinsic adhesion properties on the basis of its comparable higher crystallinity.

Bending tests are performed by attempting to bend the coated electrode around a roll of 1 cm diameter. It was found that the electrodes showed no delamination and cracks up to the thickness of 125 $\mu$m.

Swelling test is often used to characterize the mechanical properties of separators/polymers. The sample is immersed in the typical electrolyte in order to study the change in the mechanical properties in comparison to the dry sample. The separators show a volume expansion coming along with a reduction of the mechanical properties resulting from solvent penetration into the polymer host. Subsequently this leads to an increase of the total thickness of electrodes, separators and complete cells. Swelling of anode is often associated to microscopic stress due to lattice expansion anode electrode during intercalation-deintercalation.[8] Some investigations regarding the anode swelling, physical and/or electrochemical swelling, have been already performed.[7,12,13]

To analyze the swelling behavior of an electrode, the use of a capacitance measurement method has the advantage of measuring the swelling of a polymer film or composite electrodes contact-free and with high accuracy. The schematic diagram is shown in Fig. 2.

The distance between the electrode and sensor decreases after soaking the solvent into the electrode. The expansion caused by swelling can be calculated as follows:

$$Expansion(\%) = \frac{max.\ distance\ (\mu m)}{Coating\ thickness\ (\mu m)}$$

From Fig. 3 it can be seen that the crystalline binder does not show swelling behavior at all. After 220 s, even a non-conductive layer of electrolyte can be found upon the surface which is not soaked up. In contrast to the binder with high crystallinity, the binder with low crystallinity shows an uptake of 17% compared to its original thickness. The binder with medium crystallinity shows an expansion of 12% of the original thickness. Binder crystallinity directly correlates with its swelling ability. It is observed that soaking of the electrolyte into high- and medium-crystallinity binders containing anodes is not as intensive as into low crystallinity binder containing anodes. This can be explained by the polymeric microstructure (Fig. 4); due to the highly ordered structure of a crystalline polymer, solvent molecules cannot penetrate it as easily as into the disordered structure of an amorphous polymer. Polymeric microstructure also gives some possible explanations on the causes for the different electrochemical performance of the three different crystallinities. On the one hand it means that in a highly crystalline polymer only small amounts of the binder are able to perform swelling, as this only occurs in the amorphous regions.[14] Here the less swollen binder has a good ability to share electrical conductivity with the active material. On the other hand, a binder with low crystallinity has a higher amount of amorphous regions where higher

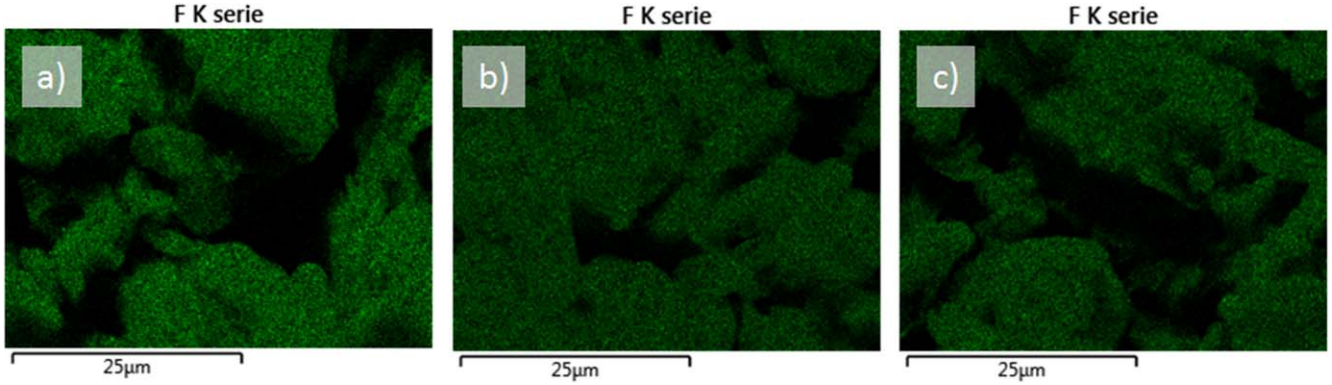


**Figure 5.** EDX image of (a) low crystallinity PVDF, (b) medium crystallinity PVDF, (c) high crystallinity PVDF.

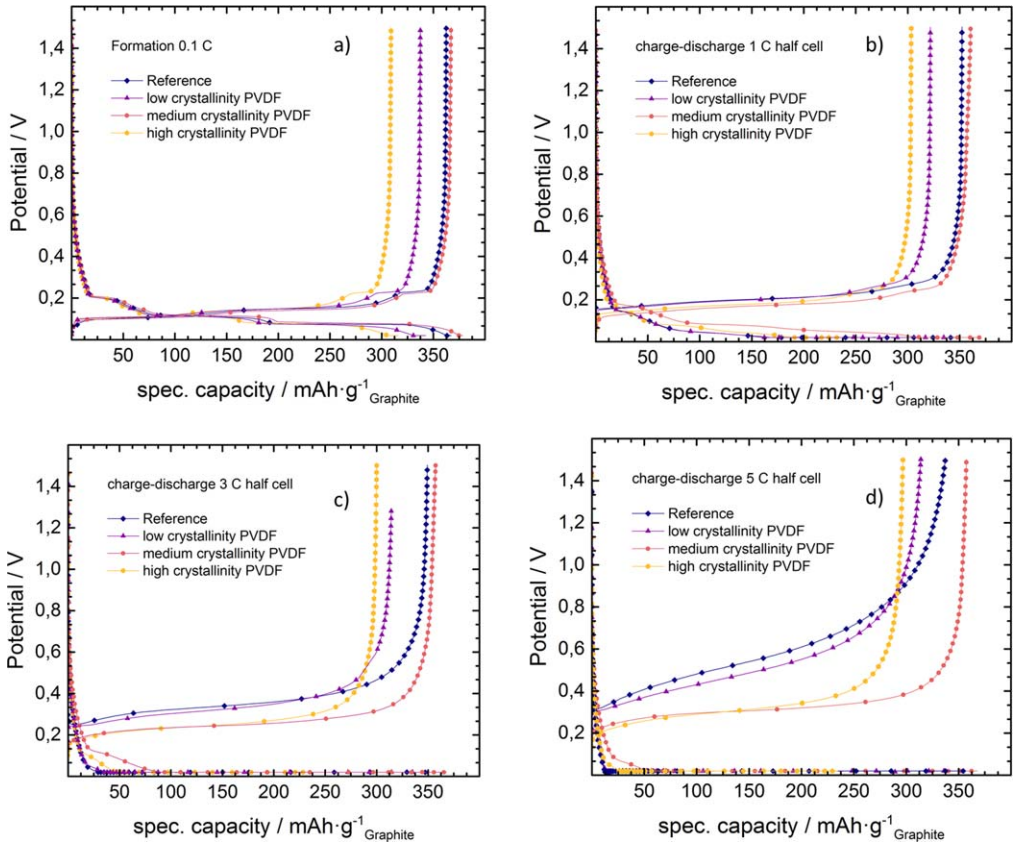


**Figure 6.** Charge-discharge profiles of graphite anodes containing different types of water based PVDF binder at different C-rates: (a) 0.1 C rate; (b) 1 C rate; (c) 3 C rate; (d) 5 C rate. Reference electrode contains SBR/CMC binder.

amounts of electrolyte can penetrate into the composite electrode to ensure good ion transport. Due to the results of electrochemical measurements, we suggest that the influence of good electrical conductivity (highly crystalline material) is little less important than a good ion transport due to good electrolyte penetration. The semi-crystalline material benefits from both influence factors and therefore shows the best results for electrochemical tests.

To check binder distribution at the surface of the composite electrode, EDX spectra have been recorded. Fluorine is used as a marker to indicate the existence of PVDF (Fig. 5). Binder distribution seems to be very homogeneous for all types of used PVDF. Also the morphologies (particle size and distribution) of the samples are similar which leads to the assumption that a comparable electrode preparation was successful.

***Half cell measurements.***—Figure 6 shows the charge-discharge curves of graphite anodes at different C-rates in the voltage range of 0.02–1.5 V where 1 C equals to 376 mA $g^{-1}$. Anode half-cells delivered discharge capacities of 362 mAh $g^{-1}$ (100%), 367 mAh $g^{-1}$ (101%), 357 mAh $g^{-1}$ (99%) and 309 mAh $g^{-1}$ (85%) at 0.1 C with reference (CMC/SBR), medium, low and high crystallinity PVDF binders, respectively. PVDF binder with medium crystallinity exhibited the slightly higher discharge capacity in comparison to the conventional water based CMC binder and other PVDF binder systems. From Fig. 8, it can be seen that CMC/SBR binder and CMC/medium crystallinity PVDF binder showed significant capacity retention upon cycling at 10 C rate, while on the other hand, low and high crystallinity PVDF binders showed negligible capacity retention at the same C-rate. CMC/SBR and PVDF binder with medium crystallinity delivered the similar capacity up to 5 C-rate.

The binder crystallinity showed a critical role on the electrochemical performance of Lithium-ion battery. The electrochemical performance of PVDF with amorphous PNVF (poly-N-vinylformamide) is compared. Amorphous PNVF binder reported a discharge capacity between 130 and 190 mAh $g^{-1}$ at 5 C and between 80 and 130 mAh $g^{-1}$ at 10 C rate.[15] These values are quite far away from the measured values of amorphous PVDF/CMC binder system with discharge capacities of 295 mAh $g^{-1}$ at 5 C and 273 mAh $g^{-1}$ at 10 C (both medium values).

The use of PVDF as binder with NMC and graphite active materials is an established and well-known technology.[16] A water-soluble PVDF binder system is a very promising option regarding

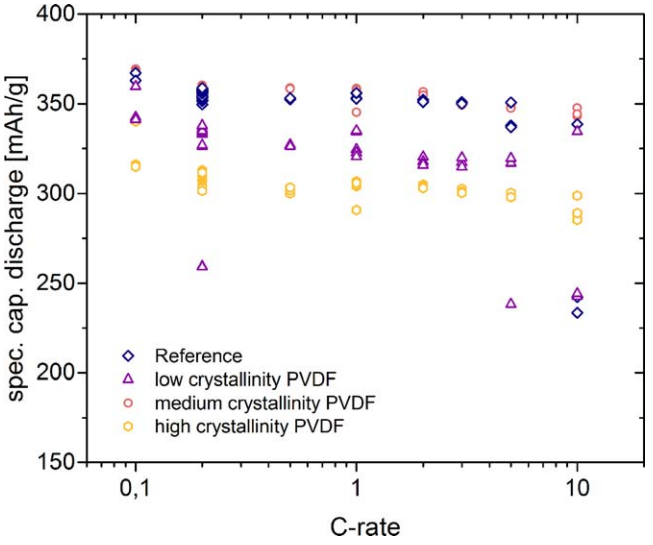


**Figure 7.** result of half-cell C-rate test

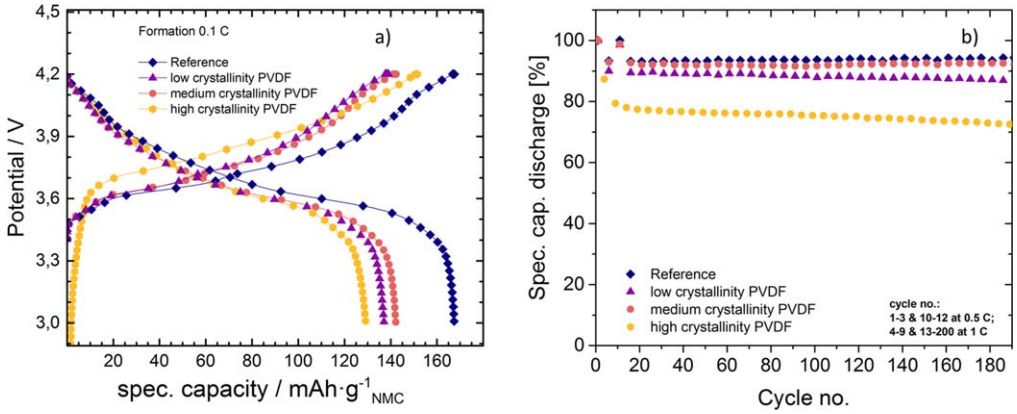


**Figure 8.** Electrochemical performance of full cells (a) charge-discharge profiles at 0.1 C rate; (b) discharge capacity data at different C-rates.

capacity retention, mechanical strength as well as positive environmental impact. From the results, it is clear that dispersed PVDF binder system with medium crystallinity exhibits good adhesion to electrode materials and current collectors (section peeling test) as well as high electrochemical stability during cycling (Figs. 6 and 7) in comparison to CMC/SBR binder. Looking at the three different types of binder systems, the performance of the medium-crystalline system is boosted by the compromise between adhesion and swelling. Several studies on NMP based PVDF binders can be found, resulting the capacities of 332 mAh $g^{-1}$ (0.1 C), 324 mAh $g^{-1}$ (0.2 C)[16] and 350–361 mAh $g^{-1}$ (0.2 C).[17] Compared to these results, the medium-crystalline Binder delivered the discharge capacity in the same range (Fig. 7, half cell C-Rate test).

When charged and discharged repeatedly, the water based binders show stable capacities over the course of several cycles at each C-rate from 0.1 C to 10 C. Half-cell tests of the investigated PVDF binder systems showed promising results concerning C-Rate stability—especially from the medium crystallinity binder. Low crystallinity binder resulted in a big variation in the capacity and capacity decreased with increasing C-Rate. The binder with high crystallinity resulted in significant capacity retention at high C-Rates, but showed the lowest capacities at different C-rates in comparison to other binder formulations. C-rate test indicates that the reference and medium crystallinity PVDF binder delivered the similar capacity >350 mAh $g^{-1}$, while high and low crystallinity binders showed slightly lower capacity >300 mAh $g^{-1}$ up to 5 C rate.

***Full cell measurements.***—Figure 8a shows the galvanostatic charge-discharge profiles of full-cells containing water-soluble binders at 0.1 C rate. Full cells delivered discharge capacities of 167 mAh $g^{-1}$ (100%), 142 mAh $g^{-1}$ (85%), 137 mAh $g^{-1}$ (82%) and 129 mAh $g^{-1}$ (77%), with reference, medium, low and high crystallinity binder systems respectively. As expected from the half-cell measurements, the full cells also delivered a comparable capacity with respect to reference binder systems. Medium crystallinity binder exhibited the highest capacity in comparison to other water-soluble PVDF binders. The cycling data of full-cells is compared in Fig. 8b. From the relative capacity graphs, it can be seen that the reference and medium crystallinity PVDF binders showed negligible capacity retention over 200 cycles. The low and high crystallinity ones showed 95% and 80% lower capacity than the binder with medium crystallinity after 150 cycles. The capacity-fading rate is varying corresponding to the crystallinity of the binder. The binder with high crystallinity showed 72% capacity fade after 200 cycles. The results are comparable to reported values obtained from a stable electrode-separator interface by lamination techniques.[18] It would be worth to mention here that lamination technique applied during the preparation of cells with water-soluble binders delivered similar discharge capacity, as has been reported,[14,18,19] by using NMP soluble PVDF binder.

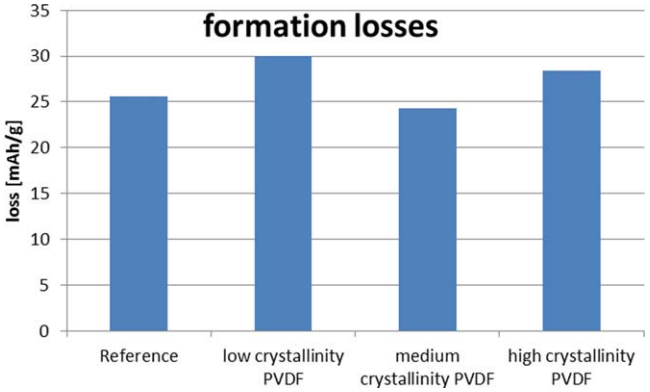


**Figure 9.** Irreversible capacity losses during formation of full cells.

Comparing the values of remaining capacity after the second formation cycle showed least formation losses for the formulation using medium crystallinity binder followed by reference formulation (Fig. 9). The values have been calculated as the difference between initial capacity and remaining capacity after the second formation cycle. The cells prepared with high and low crystallinity PVDF binder resulted in high formation losses.

## Conclusions

Graphite anodes with water-soluble CMC/SBR and CMC/PVDF binder systems are successfully coated on a copper foil by using conventional slurry and electrode roll to roll coating techniques. PVDF binders with three different crystallinities were evaluated. The prepared electrodes were tested mechanically e.g. peeling test, scratch test and electrochemically in half-cell and full cell configurations. Anode with medium crystallinity binder system showed an overall highly mechanical stable coating comparable to reference anode. Neither cycling stability nor power capability resulted in significant disadvantages compared to reference formulation.

The CMC/PVDF binder system is an environmentally friendly method with all the advantages of PVDF binder, but no explosion-proof requirements during dispersing or mixing. Further advantages covering the whole production and recycling processes as well as safety issues during operation are encouraging to do deeper research in this area.

We have introduced a novel and unique capacitance measurement method for quantification of electrode swelling which is combining several advantages like on-line measurement with direct response, easy handling and accuracy in micrometer-range. The percentage change of dry thickness in relation to the swollen thickness could be verified and showed a direct relationship between chemical structure and functionality—different crystallinities are

depicted by showing a varying degree of physical swelling. This method can also be used for characterization during the processing of anodes and cathodes as well as for swelling experiments of separators, for example.


## Acknowledgments

The Authors are thankful to Neha Ghanbahadur for assisting during measurements. This work was supported by the European Union (Project CompStor, #AB43).


## Appendix

***Capacitive displacement measurement method.—***This technique is based on the simple model of an ideal place capacitor: a sensing electrode is placed opposite to a conducting object, thus a place capacitor forms. The distance between the sensor and sample electrode is directly deduced from an impedance measurement of the capacitor. Since the impedance of a place capacitor is directly proportional to distance between its electrodes.

The capacitance $C$ of a plate capacitor is given by $C = \varepsilon\frac{A}{d}$ where $\varepsilon = \varepsilon_0\varepsilon_r$ is the permittivity of the material between the plates, composed of the permittivity of vacuum $\varepsilon_0$ and the relative permittivity of the material $\varepsilon_r$. $A$ is the area of the electrode and $d$ is the distance of the electrode to the sensor. The impedance of the system is measured in order to determine the capacitance of the sample. The magnitude of the impedance of an ideal plate capacitor is $Z = \frac{U}{I} = \frac{1}{\omega C}$ where $I$ and $\omega$ are the magnitude and the angular frequency of the applied current and $U$ is the magnitude of the voltage drop across the capacitor. The distance $d$ can now be obtained by combining the above equations:

$$d = \varepsilon\omega A\frac{U}{I}$$

Thus, the distance is directly proportional to the potential at the sensor, if the current through the system is held constant. The above theory is based on the assumption that the plate capacitor is ideal. This means that the electric field between its plates is absolutely homogeneous.

Guard electrode can be used to achieve a homogeneous field distribution in a real sensor. The guard electrode surrounds the sensing electrode and maintains the same potential. Therefore, no edge effects occur at the boundary between the two electrodes and the electric field lines are straight across the whole electrode area.

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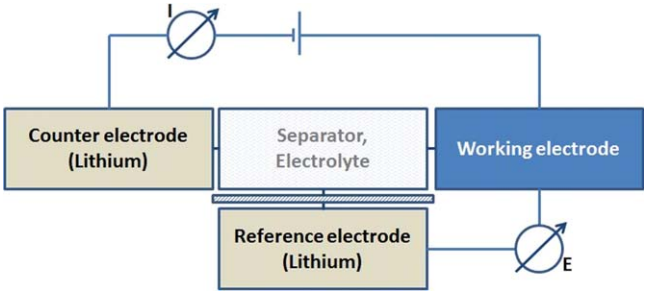


**Figure A·1.** Schematic set-up of Swagelok (c) three-electrode-arrangement.

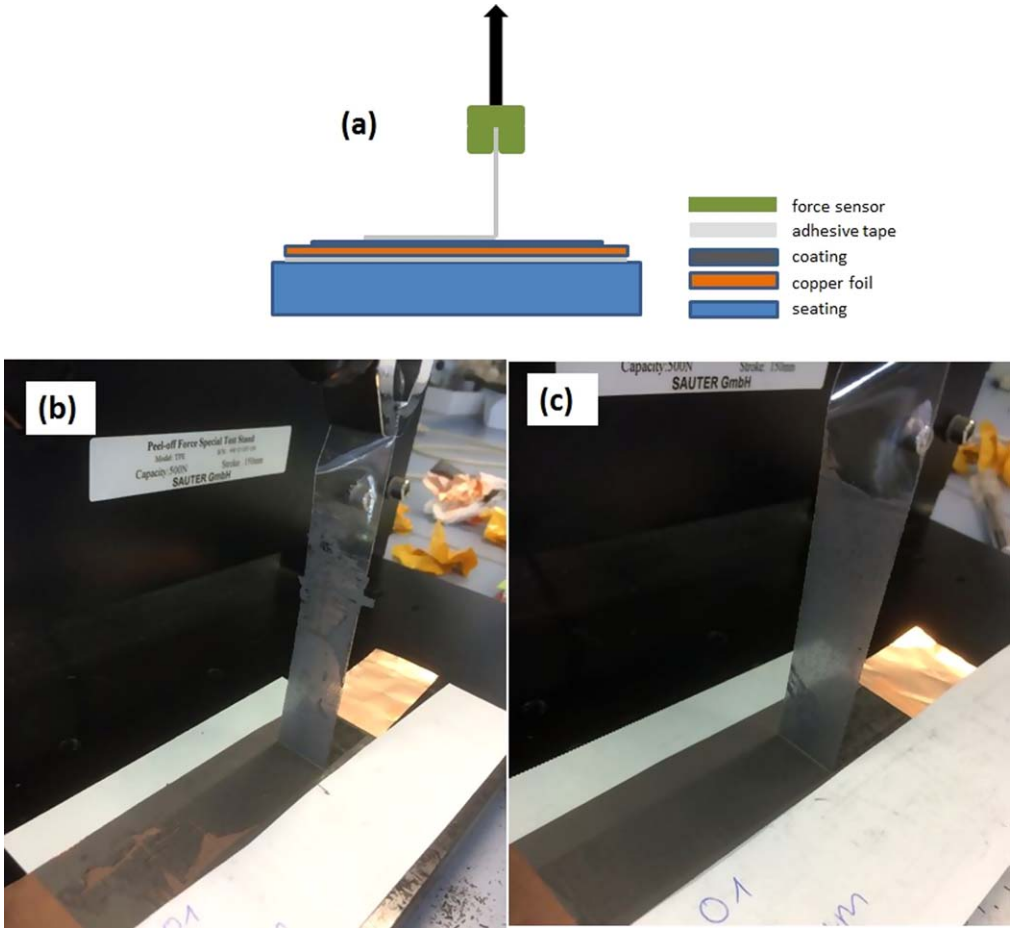


**Figure A·2.** Schematic drawing and set-up of peeling test.

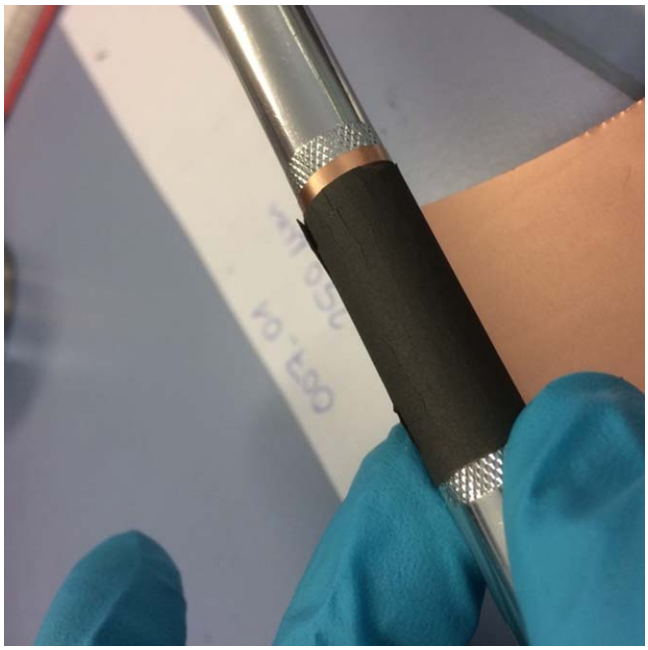

**Figure A·3.** Typical result bending test.

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