

Sorption Equilibrium and Diffusional Resistance in Compounds of Li-Ion Batteries

J. Eser^{1,2}, P. Scharfer^{1,2}, and W. Schabel^{1,2}

¹Institute of Thermal Process Engineering (TVT), Thin Film Technology (TFT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

²Material Research Center for Energy Systems (MZE), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

ISCST- 20180917PM-B-DF3

Presented at the 19th International Coating Science and Technology Symposium, September 16-19, 2018, Long Beach, CA, USA[†].

Extended Abstract

Li-ion batteries relieve daily life in their function as energy storage in many mobile and stationary applications. Ambitious aims of the German government as well as the exhaust scandal encouraged the development of more efficient and inexpensive electric vehicles in Germany. An important cost factor in the manufacturing process of Li-ion batteries poses a post-treatment in form of a subsequent drying process, what is shown in Figure 1 on the left hand side. In this process, moisture adsorbed from the air gets removed from the compounds of the battery, i.e. the electrode layers as well as the separator, by a high energy input. Otherwise, the adsorbed moisture reacts with the electrolyte in the operation of the battery, what leads to a swelling of the battery (Burns et al. 2013) and can also lead to its degeneration or a lower performance, respectively (Cuisinier et al. 2010; Zaghbi et al. 2008; Li et al. 2016).

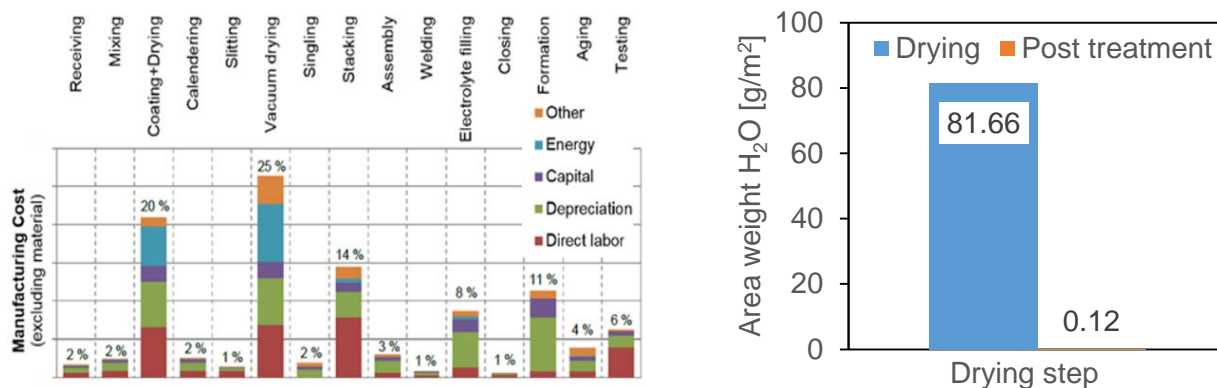


Figure 1: Manufacturing costs disregarding material costs in the process chain of a Li-Ion-battery from Schunemann et al. 2016 (left) and water to be removed in the drying steps (right).

In the literature, a connection between the long-time stability of the battery and its residual moisture content has been found. In addition to this, Zhang et al. showed that the discharge capacity of a Li-Ion-battery decreases, once the cathode material has been exposed to moisture

[†] Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

(Zhang et al. 2011). In Figure 2, the discharge capacity of a sample is compared to the sample after having been exposed to moisture.

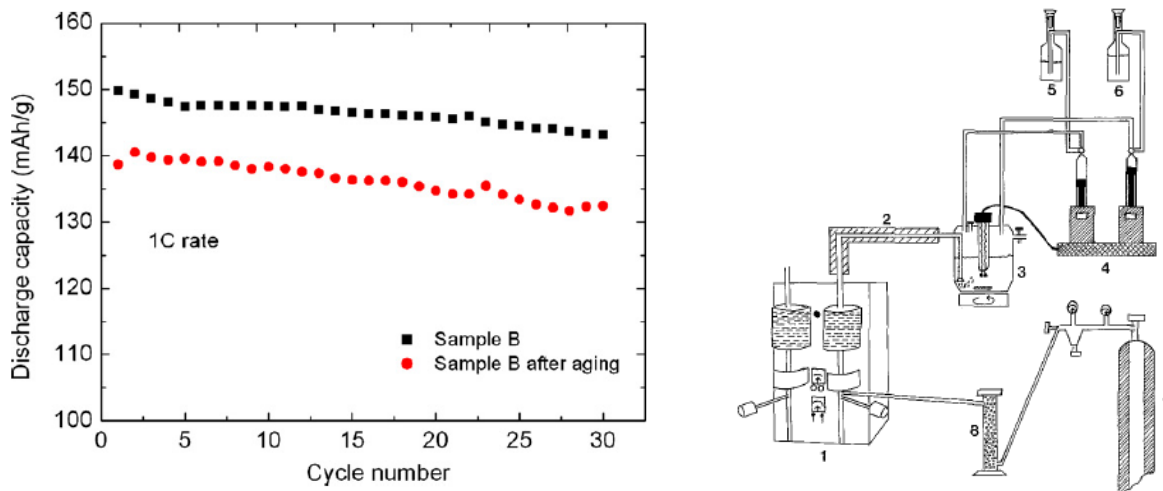


Figure 2: Decreasing discharge capacity of a Li-Ion-battery after exposure of the cathode material to moisture (red dots) from (Zhang et al. 2011) (left) and measurement principle of the jodometric Karl-Fischer titration from (Farzaneh und Troll 1977) (right).

However, the amount of water to be removed in this post-treatment is particularly small compared to the actual drying step. This is shown in Figure 1 on the right hand side, where the amount of water to be removed in the drying step is compared to the amount of water to be removed in the post-treatment. Since the water is absorbed in the binder and adsorbed in the porous structures of the components of the battery, a precise and comprehensive knowledge of the sorption equilibrium of water and the kinetics of mass transfer is necessary in order to remove the moisture cost efficiently from the compounds of the battery. A schematic representation of the process is displayed in Figure 3.

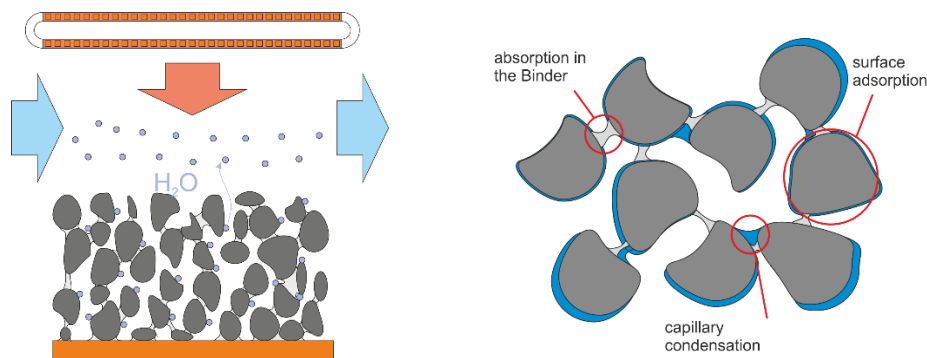


Figure 3: Schematic representation of the post-treatment process (left) and forms of moisture sorption (right).

In literature, the amount of residual moisture is usually determined by using a coulometric Karl-Fischer titration (Li et al. 2016). This method is based on a technique developed by Karl Fischer to determine the water content in sulphur dioxide (Fischer 1935) which is depicted in Figure 2 on the right hand side. However, this method of determining the water content of a sample has some disadvantages. Apart from some constructive detriments as the low contact time of the

water with the solution, it is hardly possible to associate the moisture content of the sample with different defined humidity values of the ambient conditions. This is also the reason why the history of a sample, which shows a strong hysteresis, cannot be taken into account. The sorption equilibrium, which establishes a connection between the moisture content of the sample and the humidity of the gas phase, cannot be determined.

In this work, sorption equilibria of the compounds of a Li-ion battery have been ascertained by means of a magnetic suspension balance. This gravimetric determination of the moisture content of a sample offers the advantage of adjusting a defined humidity and temperature of the sample without intervening in the measurement cell. In Figure 4, the experimental setup is shown. Here the humidity is controlled by loading a gas flow of nitrogen with water. The dewpoint is measured in a chilled mirror hygrometer afterwards and flows through the sorption cell, in which the magnetic suspension balance detects the weight of the sample continuously. By loading a gas flow with moisture, very small activities in the gas phase can be adjusted.

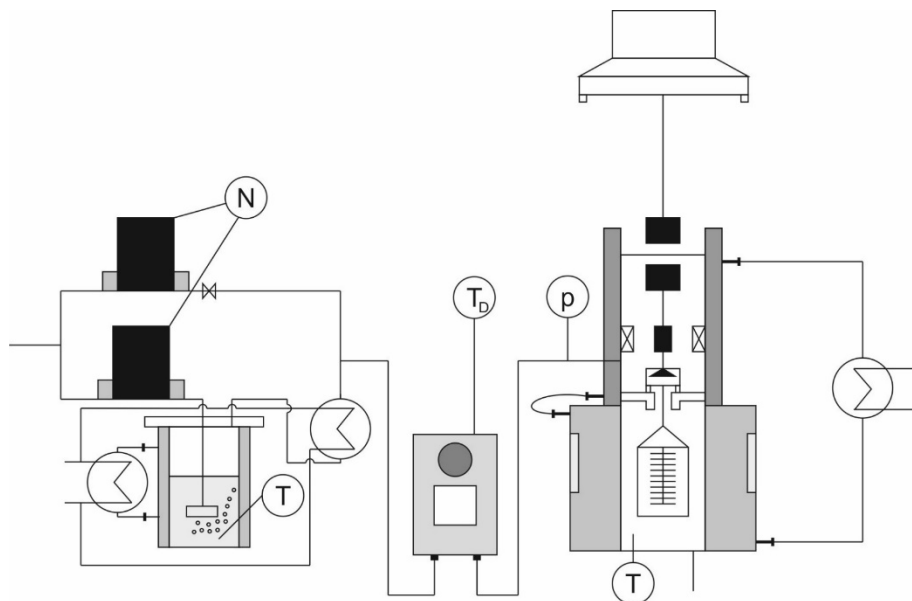


Figure 4: Sorption apparatus with chilled mirror hygrometer and magnetic suspension balance.

In addition to this, the equilibria of the particular materials of the electrodes have been investigated in order to estimate their contribution to the equilibrium of the whole electrode. The equilibria have been characterized by appropriate modelling that takes into account the requirements of the drying process such as an existing temperature-dependence.

Since the development of Li-Ion-batteries has not been completed, their material composition will change. This is why it would be advantageous to be able to describe the sorption equilibrium of the anode and cathode of the Li-Ion-battery based on the sorption equilibria of their materials. In the literature, it has been reported that the sorption equilibria of several components add up to the equilibrium of the whole structure (Kachel et al. 2013), which is shown in Figure 5.

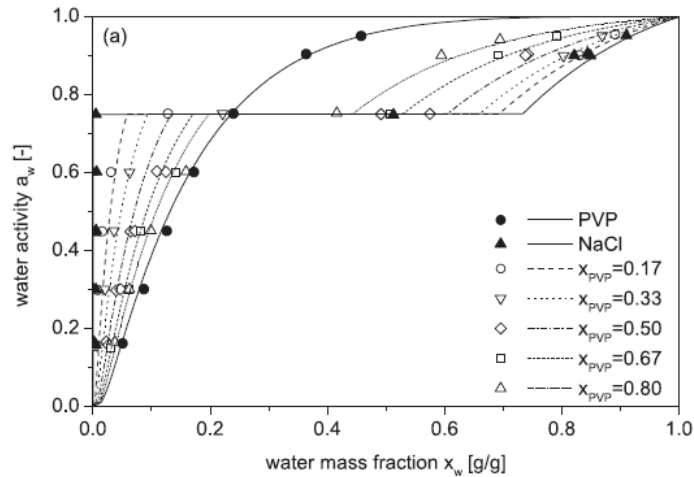


Figure 5: Sorption data from blends of PVP and NaCl described by calculation from (Kachel et al. 2013).

Part of this work is also to investigate to which amount the materials contribute to the sorption equilibrium of the electrode.

Moreover, from these experiments first conclusions have been drawn regarding the limiting diffusional resistance in the drying process. Cost-efficient reduction of the water content of the electrodes involves not only knowing their moisture adsorption and the driving force for mass transport, but also the proportionality factor of mass transport in the form of a diffusion coefficient must be known. Diffusion coefficients can be investigated by adapting the solution of the diffusion equation to the time-dependent increase in mass during individual sorption steps. This has been done previously for different materials, what is shown in Figure 6.

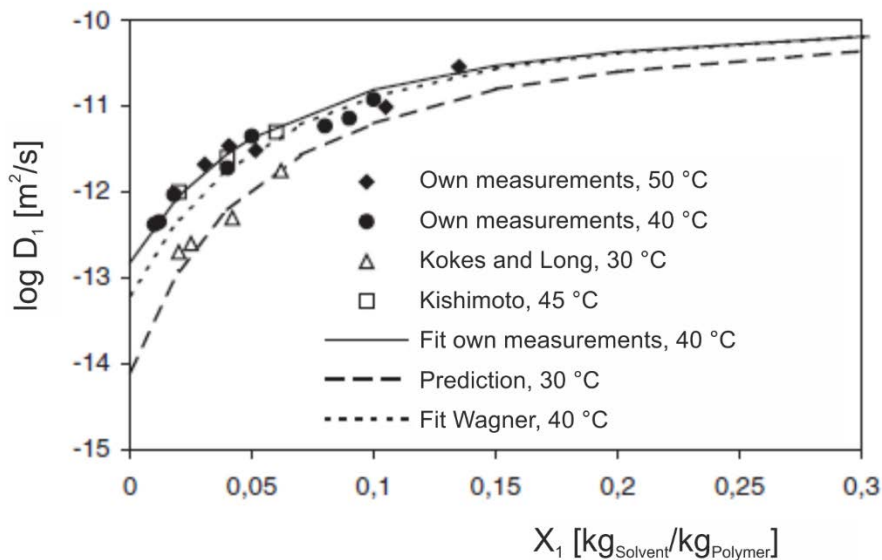


Figure 6: Diffusion coefficients of methanol in PVAc ascertained via sorption measurements from (Schabel et al. 2003).

The authors acknowledge financial support by the Federal Ministry of Education and Research via the ProCell cluster project Roll-It (contract number 03XP0080A).

Bibliography

Burns, J. C.; Sinha, N. N.; Jain, G.; Ye, H.; VanElzen, C. M.; Scott, E. et al. (2013): The Impact of Intentionally Added Water to the Electrolyte of Li-ion Cells. I. Cells with Graphite Negative Electrodes. In: *Journal of the Electrochemical Society* 160 (11), A2281-A2287. DOI: 10.1149/2.101311jes.

Cuisinier, Marine; Martin, Jean-Frédéric; Dupré, Nicolas; Yamada, Atsuo; Kanno, Ryoji; Guyomard, Dominique (2010): Moisture driven aging mechanism of LiFePO₄ subjected to air exposure. In: *Electrochemistry Communications* 12 (2), S. 238–241. DOI: 10.1016/j.elecom.2009.12.003.

Farzaneh, Abbas; Troll, Georg (1977): Quantitative Hydroxyl- und H₂O-Bestimmungsmethode für Minerale, Gesteine und andere Festkörper. In: *Z. Anal. Chem.* 287 (1), S. 43–45. DOI: 10.1007/BF00539526.

Fischer, Karl (1935): Neues Verfahren zur maßanalytischen Bestimmung des Wassergehaltes von Flüssigkeiten und festen Körpern. In: *Angewandte Chemie* 48 (26), S. 394–396.

Kachel, Sibylle; Scharfer, Philip; Schabel, Wilhelm (2013): Sorption isotherms of mixtures of polymers, proteins and electrolytes—Measurement data and model predictions. In: *Chemical Engineering and Processing: Process Intensification* 68, S. 45–54. DOI: 10.1016/j.ccep.2012.09.006.

Li, Jianlin; Daniel, Claus; An, Seong Jin; Wood, David (2016): Evaluation Residual Moisture in Lithium-Ion Battery Electrodes and Its Effect on Electrode Performance. In: *MRS Adv.* 1 (15), S. 1029–1035. DOI: 10.1557/adv.2016.6.

Schabel, W.; Mamaliga, I.; Kind, M. (2003): Messungen von Sorptionsisothermen und Diffusionskoeffizienten in Polymerlösungen. In: *Chemie Ingenieur Technik* 75 (12), S. 36–41. DOI: 10.1002/cite.200390017.

Schunemann, J.-H.; Dreger, H.; Bockholt, H.; Kwade, A. (2016): Smart Electrode Processing for Battery Cost Reduction. In: *ECS Transactions* 73 (1), S. 153–159. DOI: 10.1149/07301.0153ecst.

Zaghib, K.; Dontigny, M.; Charest, P.; Labrecque, J. F.; Guerfi, A.; Kopec, M. et al. (2008): Aging of LiFePO₄ upon exposure to H₂O. In: *Journal of Power Sources* 185 (2), S. 698–710. DOI: 10.1016/j.jpowsour.2008.08.028.

Zhang, Xiaoyu; Jiang, W. J.; Zhu, X. P.; Mauger, A.; Qilu, Julien, C. M. (2011): Aging of LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ cathode material upon exposure to H₂O. In: *Journal of Power Sources* 196 (11), S. 5102–5108. DOI: 10.1016/j.jpowsour.2011.02.009.