



Short communication

Enhanced autonomic shutdown of Li-ion batteries by polydopamine coated polyethylene microspheres



Marta Baginska^{a, b}, Benjamin J. Blaiszik^d, Tijana Rajh^d, Nancy R. Sottos^{b, c},
Scott R. White^{a, b, *}

^a Department of Aerospace Engineering, University of Illinois Urbana-Champaign, 306 Talbot Laboratory, 104 S. Wright Street, Urbana, IL 61801, USA

^b Beckman Institute for Advanced Science and Technology, University of Illinois Urbana-Champaign, 405 N. Mathews Ave, Urbana, IL 61801, USA

^c Department of Materials Science and Engineering, University of Illinois Urbana-Champaign, Materials Science and Engineering Building, 1304 W. Green St., Urbana, IL 61801, USA

^d Center for Nanoscale Materials, Argonne National Laboratory, 9700 South Cass Ave., Bldg 440, Argonne, IL 60439, USA

HIGHLIGHTS

- Polydopamine coated onto polyethylene (PE) microspheres modulates hydrophobicity.
- FTIR & Raman spectroscopy verifies polydopamine (PDA) on the microsphere surface.
- Autonomic shutdown of Li-ion coin cells is achieved using PDA-PE microspheres.
- PDA coating significantly reduces the mass of microspheres necessary for shutdown.
- Capacity loss & impedance rise confirm that shutdown has occurred upon triggering.

ARTICLE INFO

Article history:

Received 13 May 2014

Received in revised form

1 July 2014

Accepted 9 July 2014

Available online 17 July 2014

Keywords:

Li-ion batteries

Thermal shutdown

Polyethylene microspheres

Polydopamine coating

ABSTRACT

Thermally triggered autonomic shutdown of a Lithium-ion (Li-ion) battery is demonstrated using polydopamine (PDA)-coated polyethylene microspheres applied onto a battery anode. The microspheres are dispersed in a buffered 10 mM dopamine salt solution and the pH is raised to initiate the polymerization and coat the microspheres. Coated microspheres are then mixed with an aqueous binder, applied onto a battery anode surface, dried, and incorporated into Li-ion coin cells. FTIR and Raman spectroscopy are used to verify the presence of the polydopamine on the surface of the microspheres. Scanning electron microscopy is used to examine microsphere surface morphology and resulting anode coating quality. Charge and discharge capacity, as well as impedance, are measured for Li-ion coin cells as a function of microsphere content. Autonomous shutdown is achieved by applying 1.7 mg cm⁻² of PDA-coated microspheres to the electrode. The PDA coating significantly reduces the mass of microspheres for effective shutdown compared to our prior work with uncoated microspheres.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Safety of Lithium-ion batteries in electric vehicles, commercial aircraft, and consumer electronics is imperative [1–3]. To prevent catastrophic thermal failure in commercial Li-ion batteries, a

number of conventional safety devices are incorporated, including external thermal fuses, safety vents, and electronic circuit breakers [4,5]. An important concern with external safety mechanisms is the rate of response, which may be too slow to mitigate rapid internal thermal events [5]. Internal shutdown separators, i.e. polymeric films that rely on a phase change mechanism to limit ionic transport [6,7], are another commonly used safety device, but are limited in their effectiveness due to thermal shrinkage and increased risk of electrode shorting [8,9].

Previously, we have shown that thermoresponsive microspheres can be incorporated into Li-ion batteries to achieve

* Corresponding author. Department of Aerospace Engineering, University of Illinois Urbana-Champaign, 306 Talbot Laboratory, 104 S. Wright Street, Urbana, IL 61801, USA.

E-mail address: swhite@illinois.edu (S.R. White).

autonomic shutdown at a designated temperature [10]. Low density polyethylene (PE) microspheres were deposited onto a graphitic anode surface and incorporated into a Li-ion coin cell. Room temperature cycling data at 1C was identical for cells with or without microspheres. Cells containing microsphere-coated anodes were triggered for autonomic shutdown by complete immersion in silicon oil at 110 °C while cycling. Full shutdown (defined as >98% loss of initial capacity) was achieved in cells containing PE microsphere coverages greater than 7.4 mg cm^{-2} . Impedance was measured for cells before and after autonomic shutdown, and was found to increase several orders of magnitude after shutdown. While autonomic shutdown was achieved, electrode coatings were difficult to control, non-uniform in coverage, and required excess PE microspheres to achieve consistent performance.

Pure PE is a hydrophobic material, and as a result, PE microspheres do not disperse well in an *n*-methyl-2-pyrrolidone (NMP)-based binder solution. Due to the poor affinity of PE to NMP solvent, the microspheres agglomerate in solution, producing a non-uniform coating on a battery electrode.

The surface of PE can be rendered hydrophilic without altering the bulk properties of the polymer. One approach to achieving a hydrophilic surface functionalization is by polymerizing dopamine on PE. As demonstrated Ryou et al., the contact angle of water on an untreated polyethylene surface decreases from 108° to 39° degrees once the surface is treated with PDA [11]. In this work, we show that the formation of PDA on the surface of PE microspheres enhances dispersion of the microspheres in the coating solution. Improved dispersion leads to a more uniform coating of PE microspheres on the battery electrode, which in turn significantly reduces the amount of surface coverage required to achieve autonomic shutdown.

2. Results

2.1. Polydopamine coating of polyethylene microspheres

PE microspheres were prepared as described previously [10]. PDA coating was achieved using a procedure adapted from Ryou et al. [11]. Two grams of neat, dried PE microspheres were dispersed in the dopamine (10 mM) coating solution consisting of methanol and Tris buffer solution (pH 8.5) as co-solvents in a 1:1 ratio. The solution was sonicated using a tapered 3.2 mm tip of a 750 W ultrasonic homogenizer (Cole Parmer) for 2 min (pulsing at 2 s on, 0.2 s off) to improve dispersion of the microspheres in solution. The microspheres were allowed to react for 24 h under constant stirring conditions, followed by centrifuging and rinsing with DI water. Residual water was removed using a vacuum filter followed by air drying. Scanning Electron Microscope (SEM) images of the microspheres before and after coating are shown in Fig. 1a,b. The surface morphology of the polydopamine coated microspheres is significantly rougher compared to uncoated PE.

After drying, microspheres were examined using FTIR and Raman spectroscopy. The FTIR spectrum for both neat and PDA-coated microspheres are shown in Fig. 1c. The FTIR spectra obtained for neat PE microspheres is in good agreement with other low density polyethylene (LDPE) spectra obtained from literature [12]. For the PDA-coated PE microspheres, two new peaks were detected and are consistent with those observed by Ryou et al., who modified a PE separator with PDA [11]. The peak in the 1600–1650 cm^{-1} region is likely from the C–H out-of-plane bending of the benzenoid aromatic ring, while the band in the 3300 cm^{-1} region likely corresponds to the stretching vibration of free –OH, –NH₂, and C–H groups [11]. The Raman spectra for both neat PE microspheres and PDA-coated microspheres are shown in Fig. 1d. The

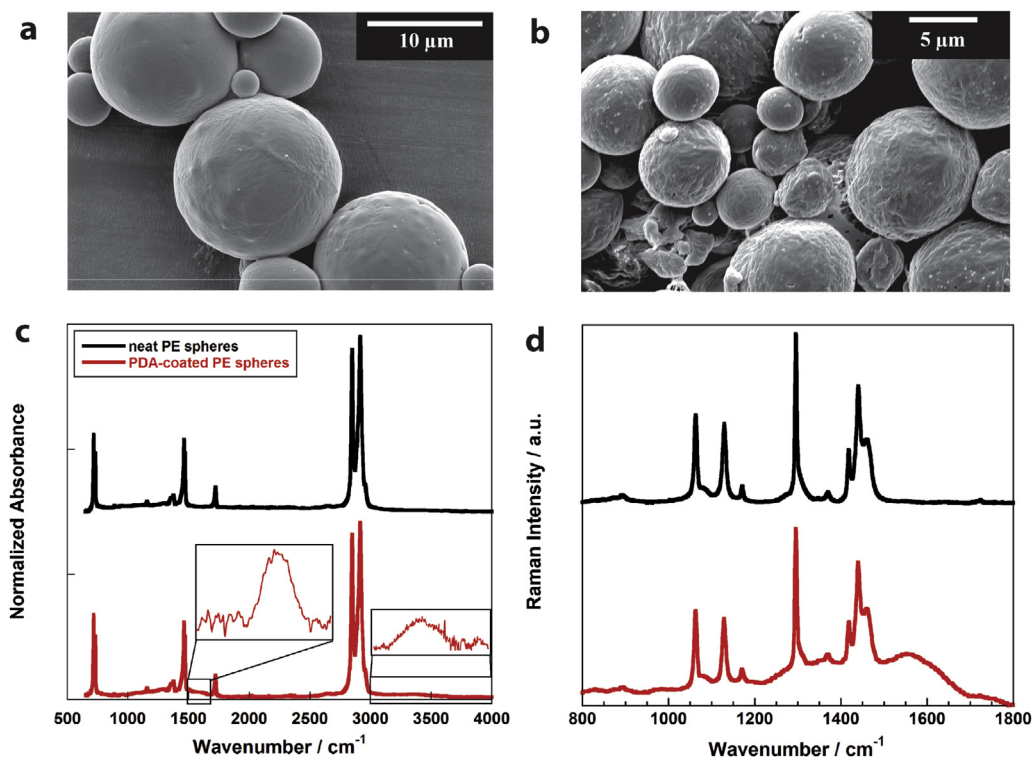


Fig. 1. Surface characterization of microspheres. (a) SEM image of uncoated PE microspheres. (b) SEM image of PDA-coated microspheres. (c) FTIR spectra of PDA-coated microspheres (red) and neat PE microspheres (black). Two new peaks emerge after PDA coating at 1600–1650 cm^{-1} and 300–3500 cm^{-1} consistent with bending and vibration signatures for PDA [11]. (d) Raman spectra for PDA-coated microspheres (red) and neat PE (black). A new broad peak at 1550 cm^{-1} emerges after coating consistent with stretching and vibration of aromatic rings [13]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Raman spectra clearly shows PDA on the sphere surface, as indicated by the peak centered between the 1550 and 1600 cm^{-1} wave numbers, characteristic of stretching and deformation of aromatic rings [13].

2.2. Coating of microspheres onto graphite anodes

We first investigated the dispersability of PDA-coated microspheres in NMP. Solutions of both neat PE microspheres (0.1 g) and PDA-coated PE microspheres (0.1 g) in poly(vinylidene fluoride) (PVDF) (0.01 g) and NMP solvent (1 g) were prepared and examined by optical microscopy. Both neat PE microspheres (Fig. 2a) as well as PDA-coated microspheres (Fig. 2b) agglomerated in NMP, even after sonication. Low concentrations of Span 80 and Tween 20 surfactants (2.5 wt% in NMP) were also added to the PVDF:NMP solution in an attempt to improve dispersion quality with no success. Despite the PDA coating, the NMP solvent was not hydrophilic enough to yield an improvement in dispersion. The quality of the dispersion improved significantly when the PDA-coated microspheres (0.1 g) were dispersed in an aqueous binder solution comprised of 0.01 g carboxymethyl cellulose (CMC) and water (1 g) and 4 drops of a 2.5 wt% aqueous solution of Tween 20 (Fig. 2d). In contrast, mixing of neat PE microspheres in this aqueous binder

solution resulted in significant agglomeration of microspheres and poor dispersion (Fig. 2c).

Mesocarbon Microbead (MCMB) commercial battery anodes were coated with the solutions from Fig. 2a (neat PE microspheres) and Fig. 2d (PDA-coated microspheres) using a doctor blade technique. As expected, the poorly-dispersed solution containing uncoated PE microspheres resulted in PE microsphere agglomeration on the anode surface, as shown in Fig. 2e. In contrast, the coating prepared from the solution of PDA-coated microspheres shows nearly complete uniformity of coverage and very little evidence of agglomeration (Fig. 2f).

2.3. Battery cycling and autonomic shutdown testing

Coated anodes were incorporated into 2032-type coin cell batteries in an Argon-filled glovebox. $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ (Li333) and Gen 2 electrolyte (1.2 M LiFP_6 EC:EMC) were used as the cathode and electrolyte materials, respectively. The coin cells also contained a commercial film separator (Celgard 2325) to prevent shorting.

The thickness of several PDA-PE coating coverages has been measured using SEM microscopy and is tabulated in Table 1, and an SEM image of a representative PDA-PE coated anode is shown in Fig. 3b.

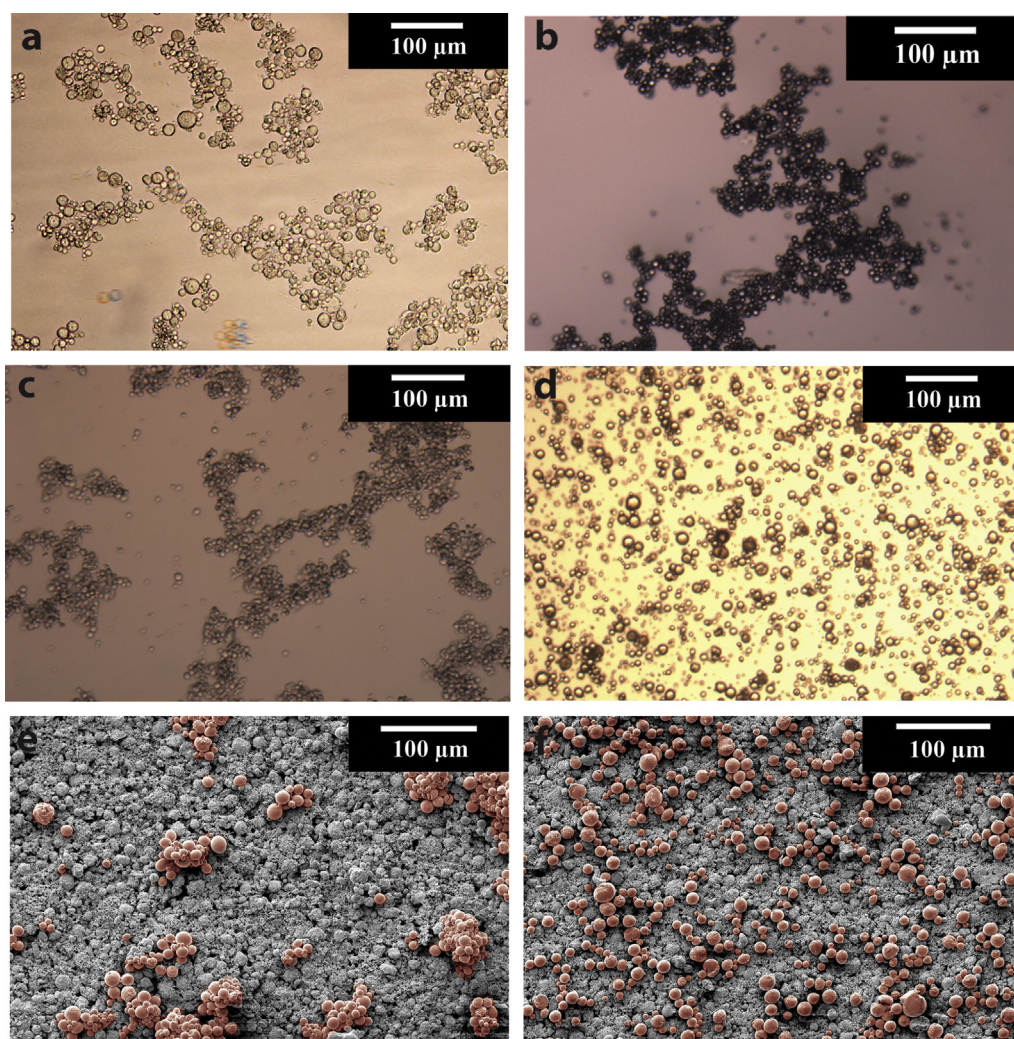


Fig. 2. Comparison of dispersion and coating uniformity of uncoated (left column) and PDA-coated (right column) PE microspheres in solution and on a battery electrode. (a) 10 wt% uncoated PE microspheres in PVDF:NMP. (b) 10 wt% PDA-coated PE microspheres in PVDF:NMP. (c) 10 wt% uncoated PE microspheres in CMC:H₂O. (d) 10 wt% PDA-coated microspheres in CMC:H₂O. (e) MCMB anode with PE microspheres applied from solution in (a). (f) MCMB anode with PDA-coated microspheres applied from solution in (d).

Table 1

Coating thickness of several surface coverages as measured by SEM.

PDA-PE coverage [mg cm^{-2}]	Coating thickness [μm]
1.5	32.5 ± 6
3.0	56.4 ± 16.7
4.7	131 ± 18.5

Cell capacity (at 1C) was measured both at room temperature (25°C), and while the cell was immersed in hot silicone oil (110°C) to activate the thermal shutdown mechanism. At room temperature, no significant capacity loss is observed at a 1C cycling rate for coin cells containing anodes with PDA-coated PE microspheres. To initiate autonomic shutdown, a temperature of 110°C was selected to ensure that the PE microspheres (m.p. 105°C by DSC) are fully melted in the battery cell. Cells were immersed in hot silicone oil for 1 min prior to cycling. A summary of these cycling results is shown in Fig. 3a.

Additionally, coin cells containing a commercial separator film were prepared, heated to 135°C to thermally activate the separator, and the remaining capacity after shutdown was measured at room temperature. On average, approximately 5% of the initial (room temperature) capacity remains after shutdown. Similarly, we define autonomic shutdown in coin cells containing PDA-coated PE spheres when 95% loss of capacity is achieved after thermal

Table 2

Room temperature impedance of PDA-PE microsphere coatings.

PDA-PE coverage [mg cm^{-2}]	Area-specific impedance [Ωcm^2]
0.0	8.1
1.2–1.5	8.5 ± 0.2
2.6	9.4
3.5–3.7	10.2 ± 0.1
6	22.2

exposure (see demarcation lines overlaid on Fig. 3a). Autonomic shutdown at 110°C is achieved for coverages ca. 1.7 mg cm^{-2} and above for coin cells with PDA-coated microspheres. This represents a reduction of 67% compared to the required coverage for coin cells using neat PE microspheres (ca. 5.1 mg cm^{-2}).

Impedance was measured for coin cells with various coverages of PDA-coated PE microspheres both before and after autonomic shutdown over a frequency range of 0.05 Hz–100 kHz (CH Instruments Model 660 Electrochemical Workstation). Area-specific impedance (ASI) at a frequency of 1 kHz (Fig. 3c) for each coverage is plotted and used as a shutdown metric. At room temperature, the presence of the PDA-PE microspheres slightly increases the impedance (ca. 5%) of the anode for coatings near the critical coverage required for shutdown (1.7 mg cm^{-2}), although the impedance increase is much more prominent at higher coverages (ca. 6 mg cm^{-2}) (Table 2).

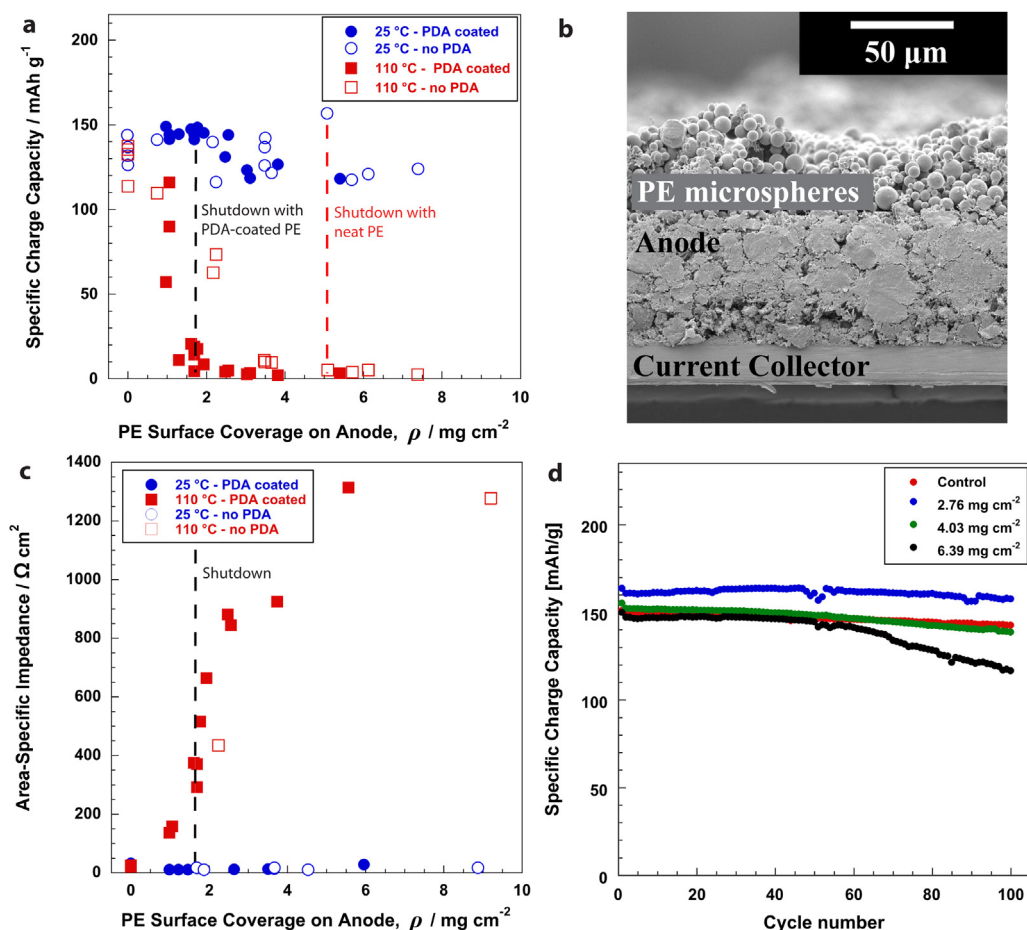


Fig. 3. Room temperature and shutdown performance of Li-ion batteries containing PDA-coated PE microspheres. (a) Capacity data for coin cells containing neat and PDA-coated PE microspheres cycled at room temperature and at 110°C . The dashed line indicates the coverage of PDA-coated microspheres at which 95% loss of capacity is achieved after thermal exposure. (b) Cross-sectional SEM image of an anode coated with PDA-PE microspheres ($\rho = 1.6 \text{ mg cm}^{-2}$). (c) Impedance data for coin cells containing neat and PDA-coated PE microspheres before and after autonomic shutdown. (d) Long term cycling data for coin cells containing anodes with various coverages of PDA-PE microspheres.

However, after cycling at 110 °C and initiating autonomic shutdown, impedance increases rapidly above 1.7 mg cm⁻² and begins to level off after the critical coverage for shutdown.

The long-term cycling capacity was examined for coin cells containing various coverages of PDA-PA microspheres on the anode surface (Fig. 3d). Cycling capacity is very stable for 100 cycles in coin cells that contained a coverage less than 6.39 mg cm⁻². This cycling data also demonstrates that the aqueous-based coating methods of the anode are compatible with standard carbon anodes prepared with PVDF binder dissolved with NMP.

3. Conclusions

PE microspheres were coated with PDA to improve dispersion of the microspheres in an aqueous binder solution and enable uniform dispersion onto MCMB battery anodes. Autonomic shutdown of Li-ion coin cells was demonstrated by submerging the cells in silicone oil held at 110 °C. Using both capacity loss and impedance rise, it was demonstrated that using PDA-coated PE microspheres reduces the amount of applied spheres necessary for shutdown by 67% compared to uncoated PE microspheres.

Acknowledgments

This research was supported as part of the Center for Electrical Energy Storage, an Energy Frontier Research Center funded by the

US Department of Energy, Office of Science, Office of Basic Energy Sciences. M. Baginska would also like to acknowledge the National Science Foundation for its Graduate Research Fellowship Program (GRFP) Fellowship. B. Blaiszik was supported via the Argonne National Laboratory Director's Postdoctoral Fellowship. The authors would like to thank Dr. Chris Johnson at Argonne National Laboratory for allowing the use of the CH instruments potentiostat in his lab and Dr. David Schilter (UIUC) for assistance with FTIR experiments.

References

- [1] B. Smith, Chevrolet Volt Battery Incident Overview Report, National Highway Traffic Safety Administration, 2012.
- [2] Interim Factual Report, National Transportation Safety Board, Office Of Aviation Safety, Washington, DC, 2013.
- [3] C. Mikolajczak, M. Kahn, K. White, R.T. Long, Lithium-ion Batteries Hazard and Use Assessment, The Fire Protection Research Foundation, 2011.
- [4] P.G. Balakrishnan, R. Ramesh, T. Prem Kumar, J. Power Sources 155 (2006) 401.
- [5] G. Venugopal, J. Power Sources 101 (2001) 231.
- [6] P. Arora, Z. Zhang, Chem. Rev. 104 (2004) 4419.
- [7] X. Huang, J. Solid State Electrochem. 15 (2010) 649.
- [8] E.P. Roth, D.H. Doughty, D.L. Pile, J. Power Sources 174 (2007) 579.
- [9] Y.S. Chung, S.H. Yoo, C.K. Kim, Ind. Eng. Chem. Res. 48 (2009) 4346.
- [10] M. Baginska, B.J. Blaiszik, R.J. Merriman, N.R. Sottos, J.S. Moore, S.R. White, Adv. Energy Mater. 2 (2012) 497.
- [11] M.-H. Ryou, Y.M. Lee, J.-K. Park, J.W. Choi, Adv. Mater. 23 (2011) 3066.
- [12] J. Gulmine, P. Janissek, H. Heise, L. Akcelrud, Polym. Test. 21 (2002) 557.
- [13] W. Ye, D. Wang, H. Zhang, F. Zhou, W. Liu, Electrochim. Acta 55 (2010) 2004.