Supporting Information

Polypyrenes as High-Performance Cathode Materials for Aluminum Batteries

Marc Walter,[†,‡,#] Kostiantyn V. Kravchyk,[†,‡,#] Cornelia Böfer, [†,‡] Roland Widmer, [£] and Maksym V. Kovalenko[,†,‡]*

Dr. M. Walter, Dr. K. V. Kravchyk, C. Böfer, Prof. Dr. M. V. Kovalenko

[†] Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 1, CH-8093 Zürich, Switzerland

[‡] Laboratory for Thin Films and Photovoltaics, Empa – Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

Dr. Roland Widmer

[£] Nanotech@surfaces Laboratory, Empa – Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

[*]E-mail: mvkovalenko@ethz.ch
[#]Equal contributions

Keywords: Energy storage, aluminum batteries, pyrene, polypyrenes.

Calculation of theoretical gravimetric capacity of pyrene

Gravimetric capacity (C, in mAh g^{-1}) of an electrochemically active material can be calculated using the as follows:

$$C = \frac{x*F}{M} \qquad (1)$$

where $F = 26.8 \cdot 10^3$ mAh mol^{-1} (Faraday constant); x = number of electrons (in mols) used to oxidize/reduce 1 mol of the active material, M – molar mass of active material in g mol^{-1};

The theoretical capacity of pyrene is calculated based on a one-electron process per pyrene unit:

$$C = \frac{1*F}{202.25} \approx 133 \text{ mAh } g^{-1} \qquad (2)$$

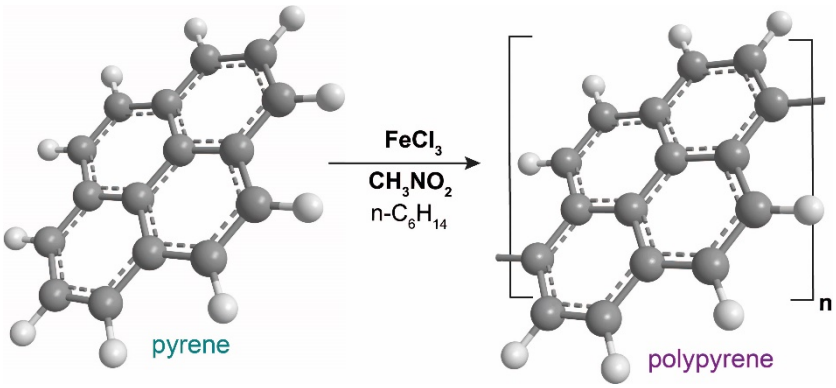

Figure S1. Reaction scheme for the synthesis of polypyrene according to Li *et al*.[1]

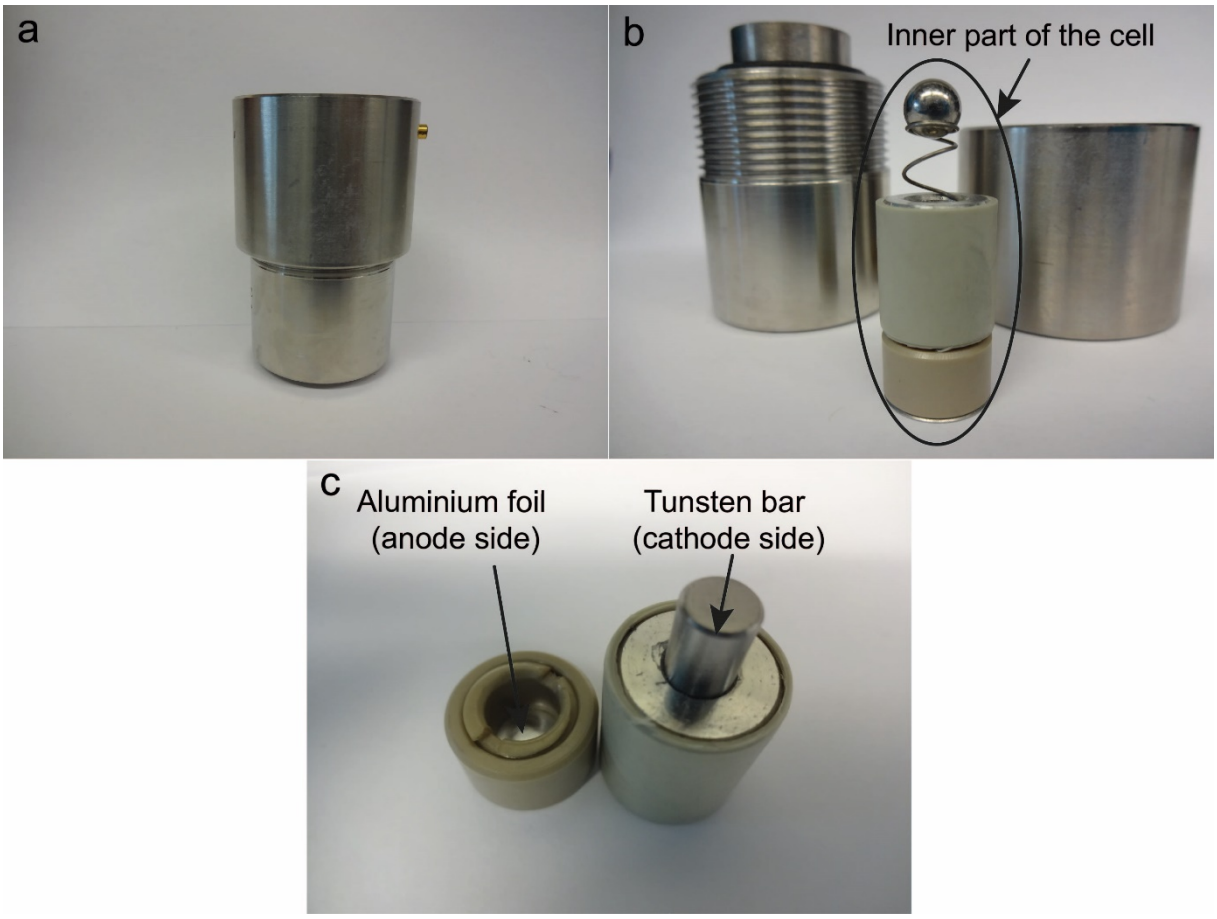

Figure S2. Custom-made cell used for electrochemical measurements.

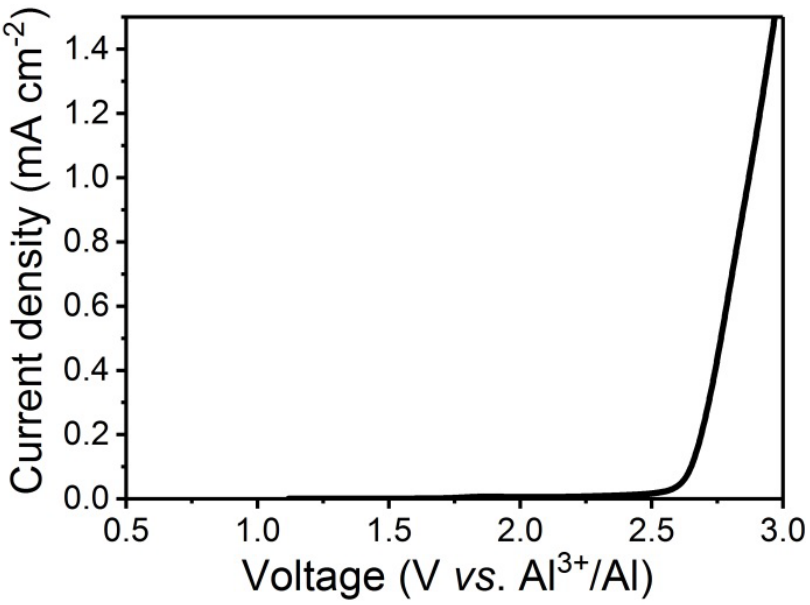

Figure S3. Cyclic voltammetry curve for tungsten current collector measured in $AlCl_3$-[EMIm]Cl ionic liquid (2:1 mol. ratio) at a rate of 10 mV s^{-1}.

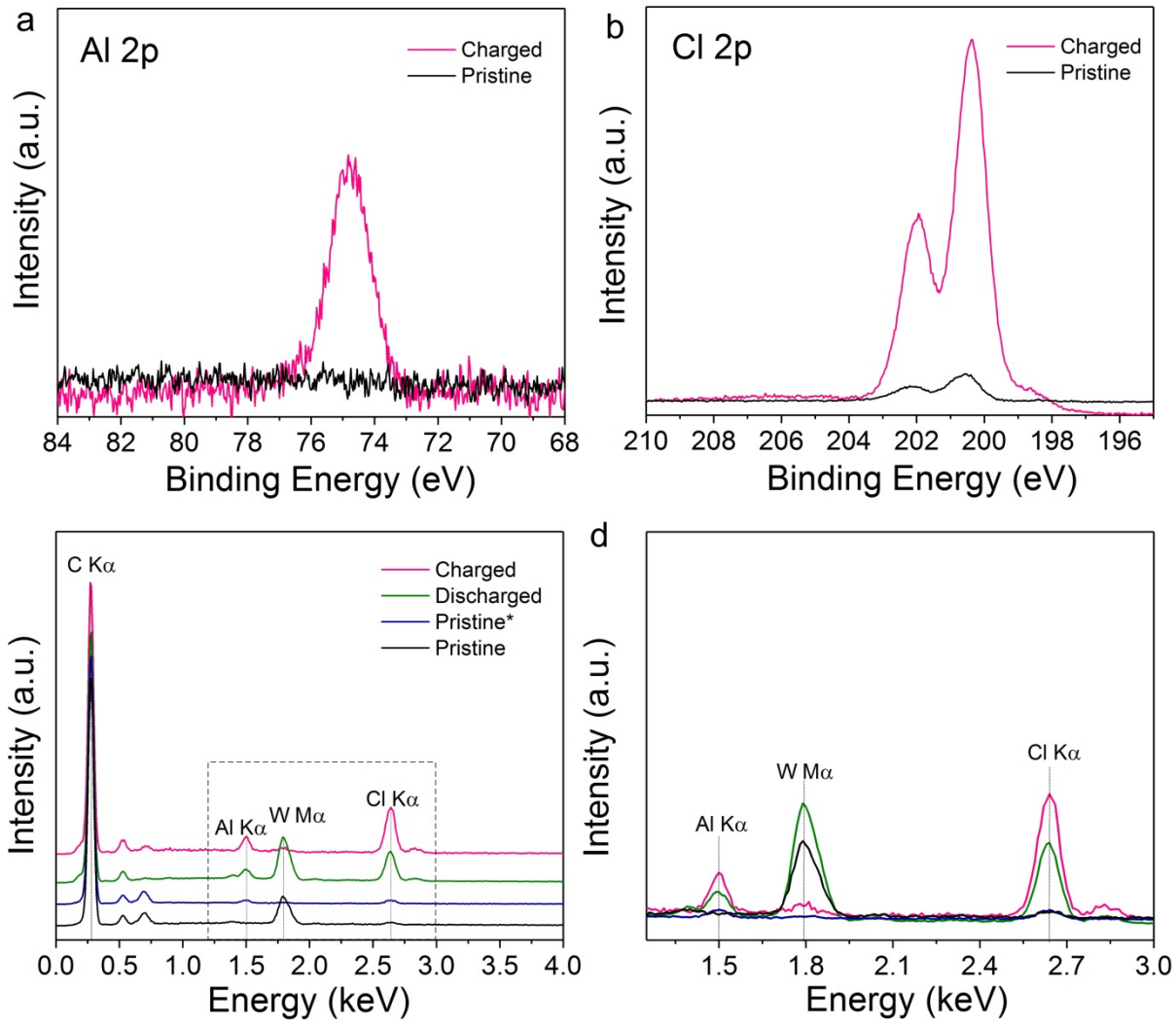

Figure S4. Detail XP spectra of (a) Al 2p and (b) Cl 2p of charged and pristine polypyrene electrodes. (c, d) EDX spectra of charged, discharged, pristine* and pristine electrodes (figure d shows comparison of intensities of Al Kα and Cl Kα peaks normalized by the intensity of C Kα peak). Charged and discharged electrodes were prepared by electrochemical charging or discharging of polypyrene electrodes at current density of 200 mA g^{-1} (2^{nd} cycle), followed by washing with anhydrous acetonitrile (ACN) as an oxidatively stable solvent capable of removing the ionic liquid. Sample designated as Pristine* was prepared by impregnation of polypyrene electrode in $AlCl_3$:EMIMCl electrolyte, followed by washing with ACN. Small intensity of Al Kα and Cl Kα peaks after the washing procedure for Pristine* sample confirms removal of chloroaluminate ionic liquid from the surface of polypyrene electrode. The remaining Al Kα and Cl Kα peaks for discharged sample can be attributed to the trapped $AlCl_4^-$ ions after the first charge.

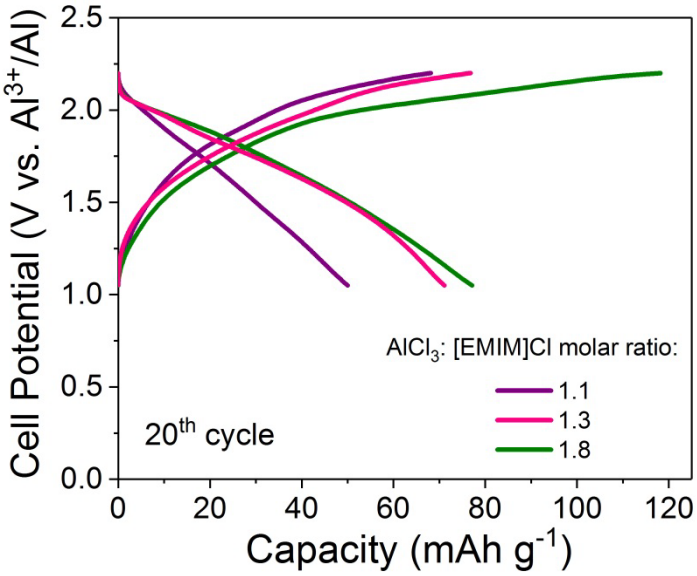

Figure S5. Charge/discharge voltage profiles for the 20th cycle of a polypyrene cathode at various molar ratios of $AlCl_3$:EMIMCl ionic liquid (1.1, 1.3, 1.8). Cells were cycled at room temperature at a current density of 200 mA g^{-1} (referring to the mass of the polymer) in the potential range of 1.05–2.2 V.

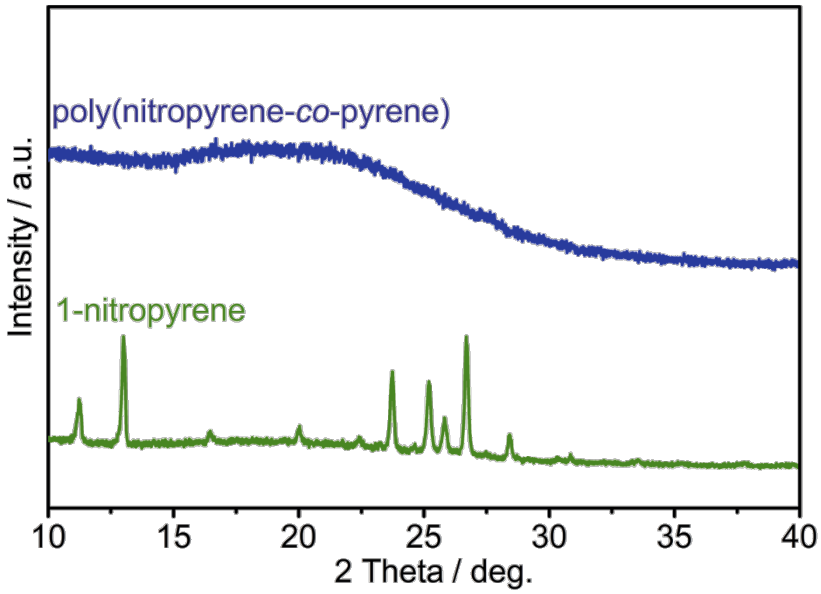

Figure S6. Comparison of the XRD patterns of poly(nitropyrene-*co*-pyrene) and 1-nitropyrene).

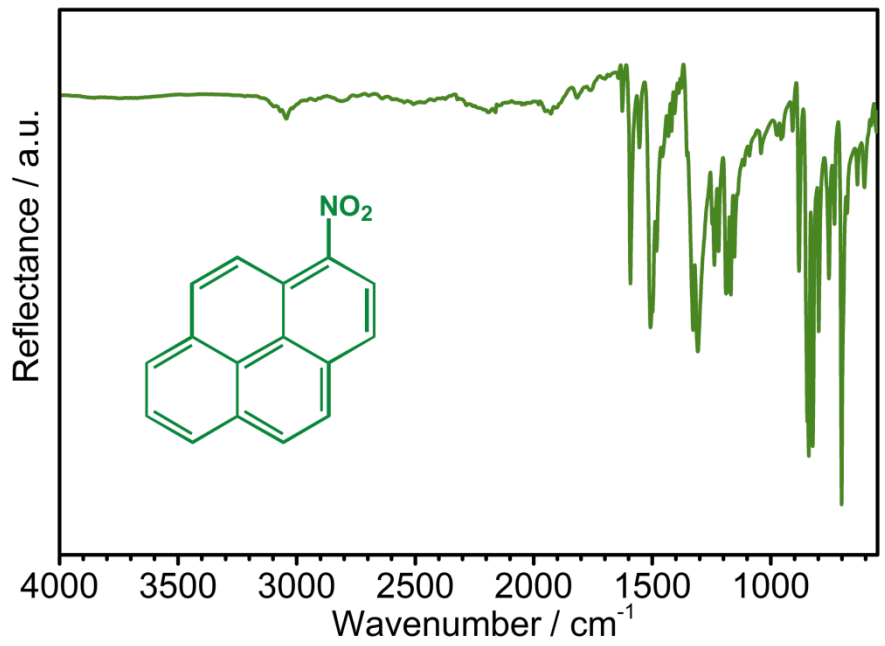

Figure S7. FTIR-spectrum of 1-nitropyrene.

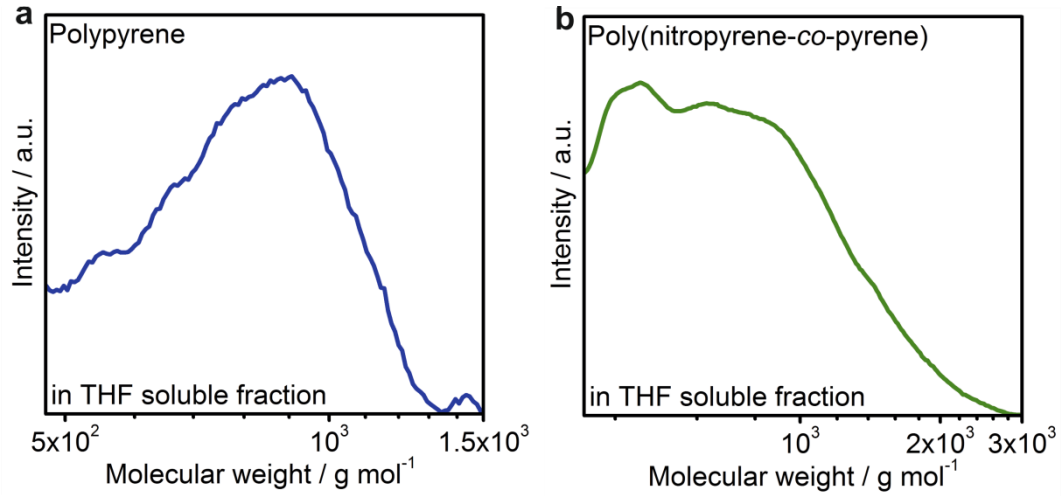

Figure S8. Gel permeation chromatography in THF soluble fractions of (a) polypyrene and (b) poly(nitropyrene-*co*-pyrene).

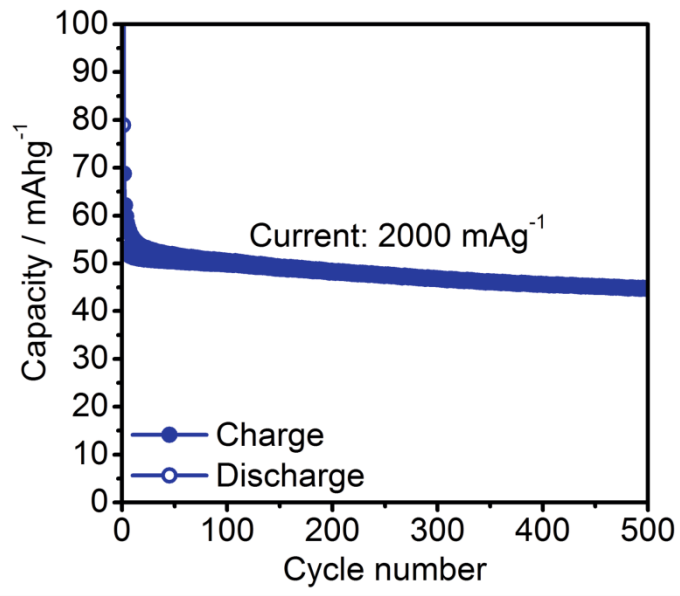

Figure S9. Capacity retention of poly(nitropyrene-*co*-pyrene) as cathode material in aluminum battery. Cells were cycled at room temperature with a current density of 2000 mA g^{-1} in the potential range of 1.05–2.2 V.

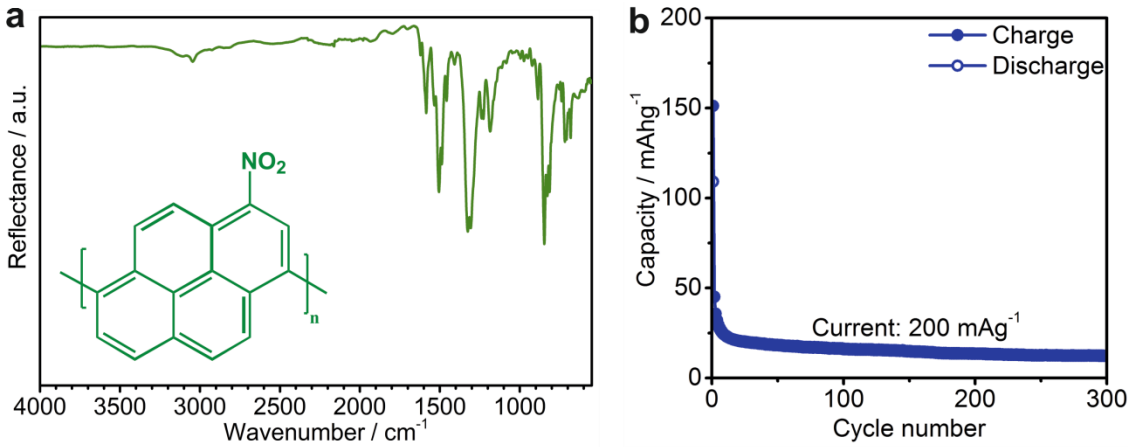

Figure S10. (a) FTIR-spectrum and (b) capacity retention for polynitropyrene prepared using the same conditions as for polypyrene and poly(nitropyrene-*co*-pyrene) with only 1-nitropyrene as starting material. Cells were cycled at room temperature with a current density of 200 mA g^{-1} in the potential range of 1.05–2.2 V.

Table S1. Comparison of the electrochemical performance of the herein presented polypyrene and with other polymeric materials reported as cathode materials for aluminum batteries.

Cathode material	Current density	Average capacity	Cycle number	Average discharge voltage
Poly(nitropyrene-*co*-pyrene)	200 mA g^{-1}	100 mAh g^{-1}	500	~1.7 V
(present work)		94 mAh g^{-1}	1000	~1.7 V
Polypyrrole[2]	20 mA g^{-1}	~55 mAh g^{-1}	100	~1.2 V
Polythiophene[2]	16 mA g^{-1}	~75 mAh g^{-1}	100	~1.4 V

References

1. X.-G. Li , Y.-W. Liu, M.-R. Huang, S. Peng, L.-Z. Gong and M. G. Moloney, *Chem. - Eur. J.*, 2010, **16**, 4803-4813.
2. N. S. Hudak, *J. Phys. Chem. C*, 2014, **118**, 5203-5215.