

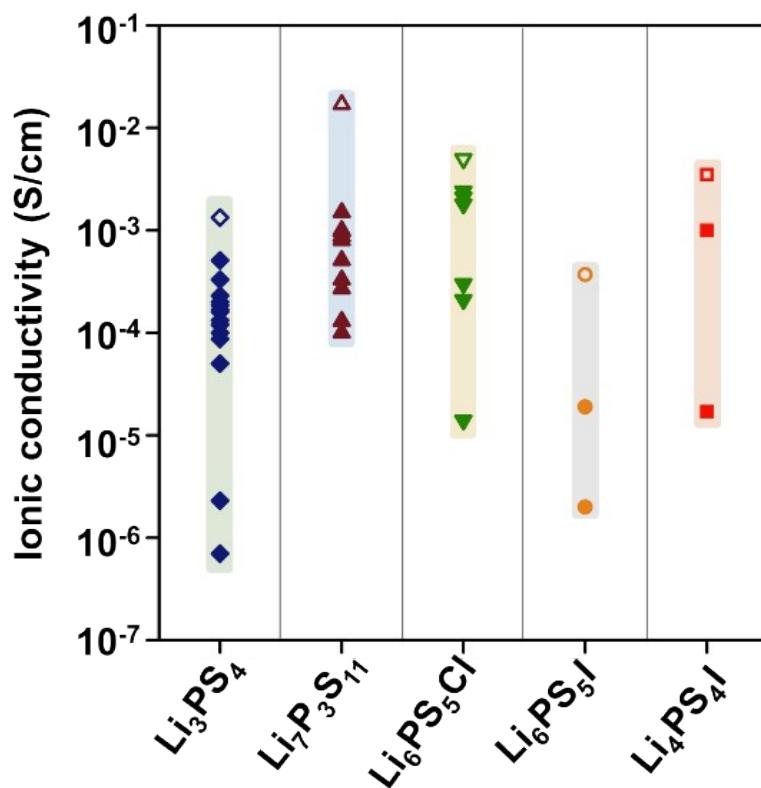
## Structural Evolution During Solution-Based Synthesis of $\text{Li}_7\text{P}_3\text{S}_{11}$ Solid Electrolyte by Synchrotron X-ray Total Scattering

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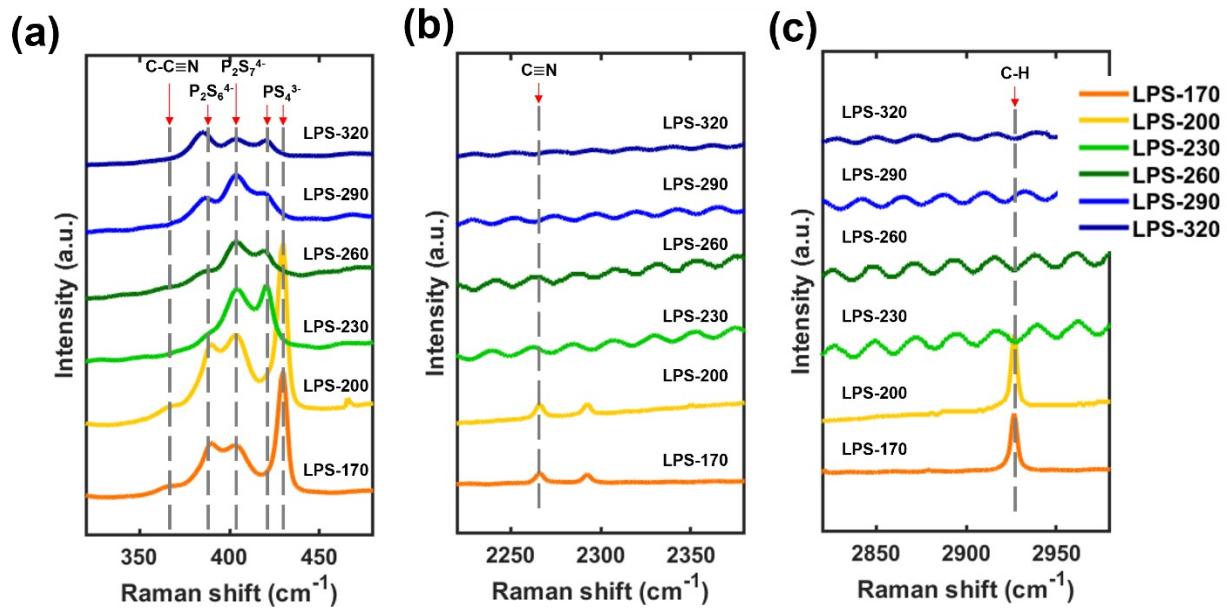
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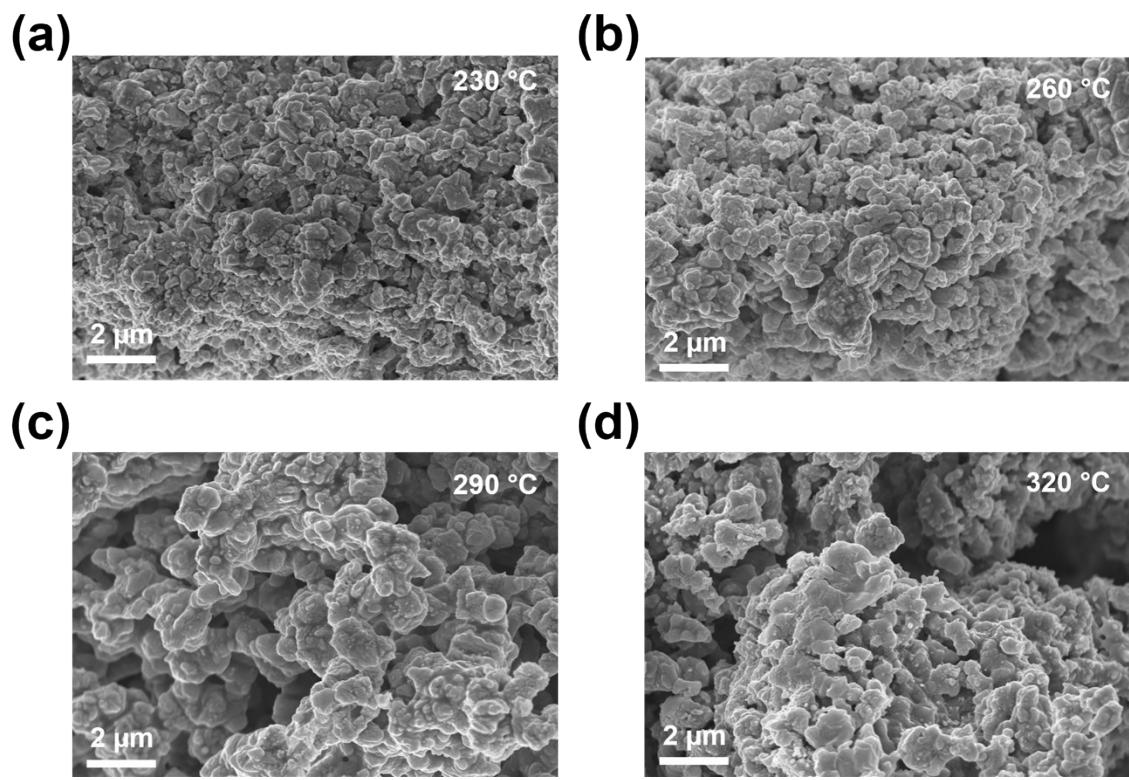
E-mail: [hanf2@rpi.edu](mailto:hanf2@rpi.edu)



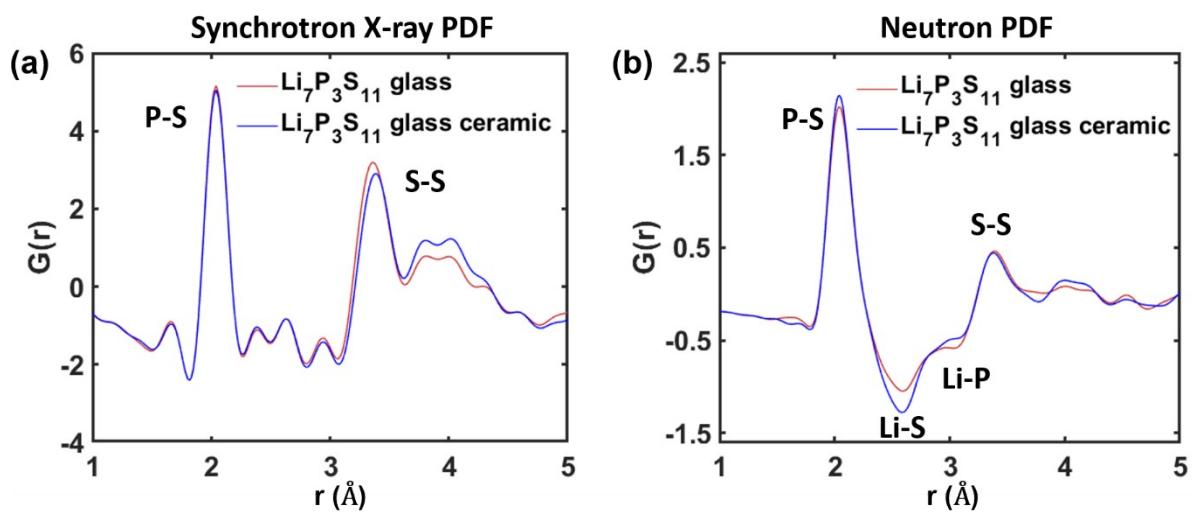
**Figure S1.** Ionic conductivities of SEs synthesized by solution method (solid symbols)<sup>1–26</sup> and by solid-state synthesis/ball-milling methods (hollow symbols).<sup>27–29</sup>



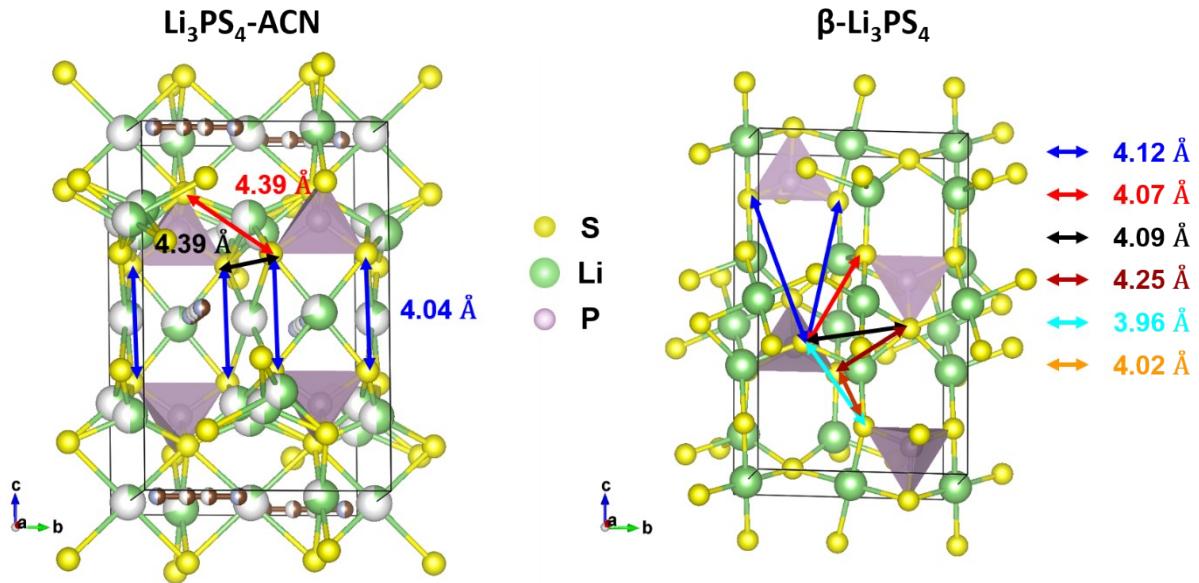
**Figure S2.** Raman spectra of SEs annealed from 170 °C to 320 °C in the range of 320-480  $\text{cm}^{-1}$  (a) 2220-2380  $\text{cm}^{-1}$  (b), and 2820-2980  $\text{cm}^{-1}$  (c).



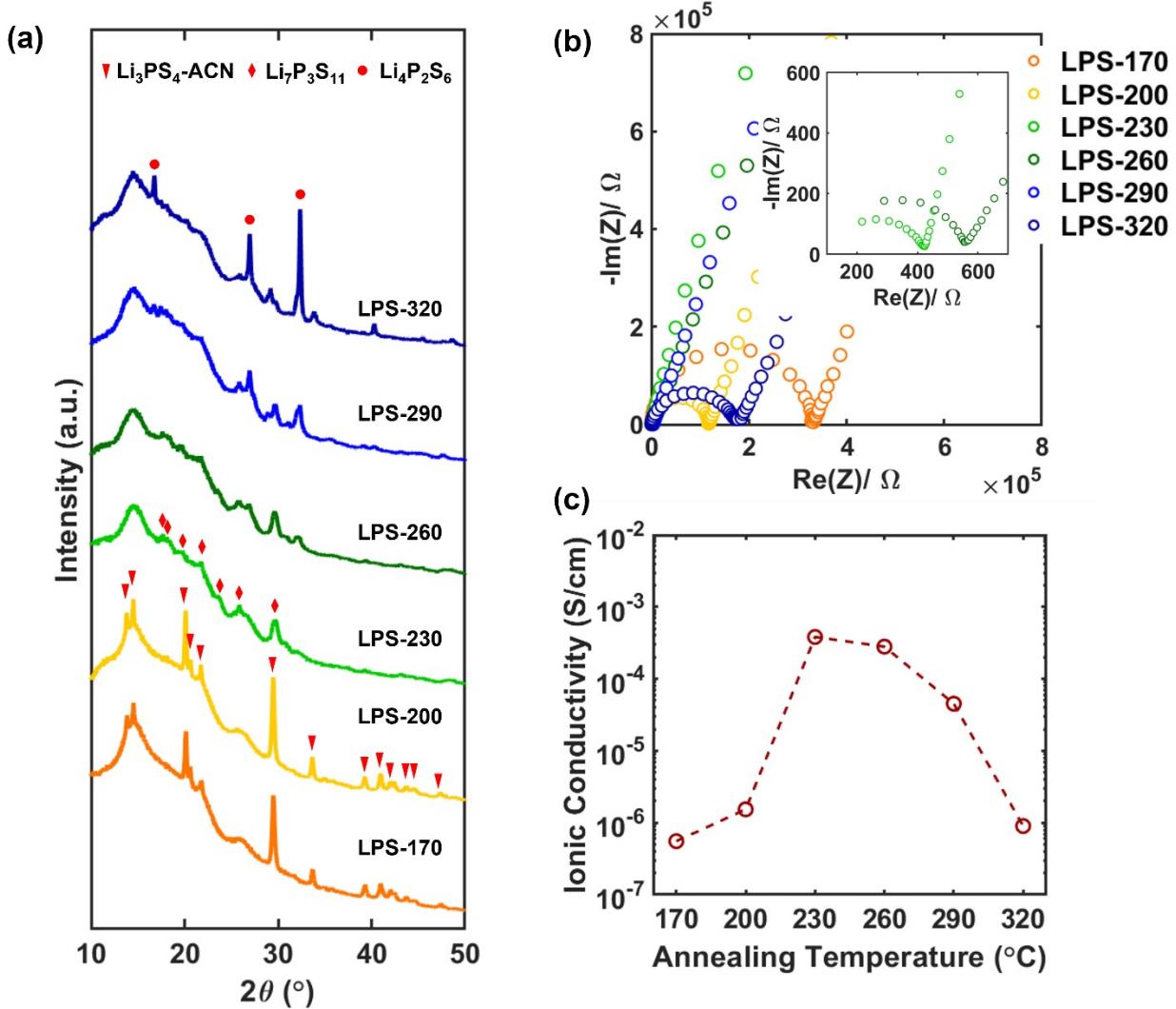
**Figure S3.** Particle morphology of SEs annealed at 230 °C (a), 260 °C (b), 290 °C (c), and 320 °C (d).



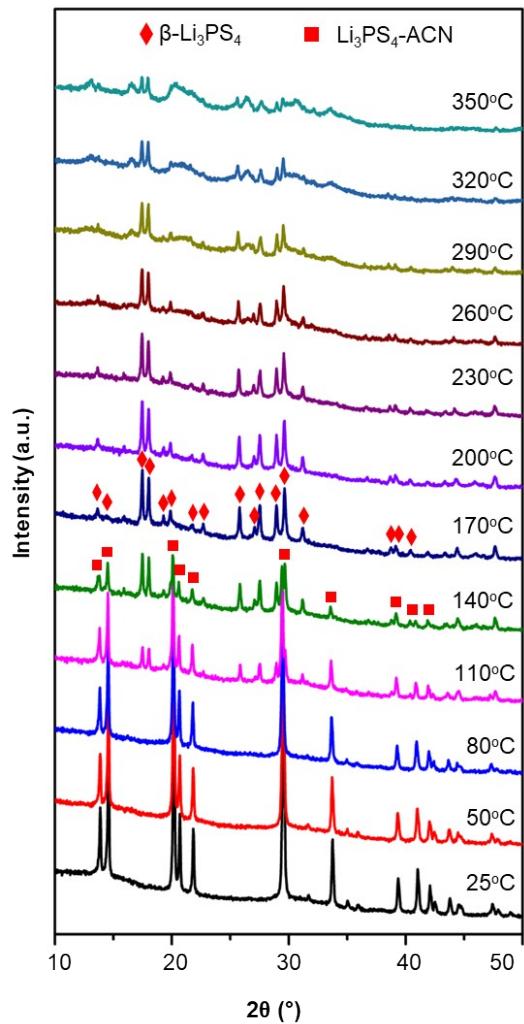
**Figure S4.** Synchrotron X-ray (a) and neutron (b) PDFs of  $\text{Li}_7\text{P}_3\text{S}_{11}$  glass and glass ceramic synthesized by ball-milling method.



**Figure S5.** (a) Structure of  $\text{Li}_3\text{PS}_4\text{-ACN}$  complex and  $\beta\text{-Li}_3\text{PS}_4$  with characteristic S-S bonds between adjacent  $\text{PS}_4^{4-}$  units. (b) Calculated reduced PDFs of  $\text{Li}_3\text{PS}_4\text{-ACN}$  complex and  $\beta\text{-Li}_3\text{PS}_4$ .



**Figure S6.** Structural and ionic conductivity measurement of SEs annealed at different temperatures for 6 hours. (a) Lab X-ray diffraction patterns of SEs synthesized after annealing at different temperatures for 6 hours. (b) Impedance plots of SEs with stainless steel blocking electrodes measured at room temperature. The impedance measurement was performed from 7 MHz to 10 mHz. (c) Room temperature ionic conductivity of SEs synthesized after annealing at different temperatures for 6 hours.



**Figure S7.** In-situ XRD patterns during vacuum annealing of solution-synthesized precursor for the synthesis of Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>.

## Reference

- 1 Y. Wang, D. Lu, M. Bowden, P. Z. El Khoury, K. S. Han, Z. D. Deng, J. Xiao, J.-G. Zhang and J. Liu, *Chem. Mater.*, 2018, **30**, 990–997.
- 2 N. H. H. Phuc, M. Totani, K. Morikawa, H. Muto and A. Matsuda, *Solid State Ion.*, 2016, **288**, 240–243.
- 3 M. Calpa, N. C. Rosero-Navarro, A. Miura and K. Tadanaga, *RSC Adv.*, 2017, **7**, 46499–46504.
- 4 S. Ito, M. Nakakita, Y. Aihara, T. Uehara and N. Machida, *J. Power Sources*, 2014, **271**, 342–345.
- 5 S. Teragawa, K. Aso, K. Tadanaga, A. Hayashi and M. Tatsumisago, *J. Mater. Chem. A*, 2014, **2**, 5095–5099.
- 6 S. Teragawa, K. Aso, K. Tadanaga, A. Hayashi and M. Tatsumisago, *J. Power Sources*, 2014, **248**, 939–942.
- 7 S. Yubuchi, S. Teragawa, K. Aso, K. Tadanaga, A. Hayashi and M. Tatsumisago, *J. Power Sources*, 2015, **293**, 941–945.
- 8 A. Matsuda, H. Muto and N. H. H. Phuc, *Jpn. Soc. Powder Powder Metall.*, 2016, **63**, 976–980.
- 9 N. H. H. Phuc, K. Morikawa, M. Totani, H. Muto and A. Matsuda, *Solid State Ion.*, 2016, **285**, 2–5.
- 10 H. Wang, Z. D. Hood, Y. Xia and C. Liang, *J. Mater. Chem. A*, 2016, **4**, 8091–8096.
- 11 R. C. Xu, X. H. Xia, Z. J. Yao, X. L. Wang, C. D. Gu and J. P. Tu, *Electrochim. Acta*, 2016, **219**, 235–240.
- 12 N. H. H. Phuc, K. Morikawa, T. Mitsuhiro, H. Muto and A. Matsuda, *Ionics*, 2017, **23**, 2061–2067.
- 13 N. H. Huy Phuc, T. Yamamoto, H. Muto and A. Matsuda, *Inorg. Chem. Front.*, 2017, **4**, 1660–1664.
- 14 S. J. Sedlmaier, S. Indris, C. Dietrich, M. Yavuz, C. Dräger, F. von Seggern, H. Sommer and J. Janek, *Chem. Mater.*, 2017, **29**, 1830–1835.
- 15 M. Calpa, N. C. Rosero-Navarro, A. Miura and K. Tadanaga, *Inorg. Chem. Front.*, 2018, **5**, 501–508.
- 16 S. Choi, S. Lee, J. Park, W. T. Nichols and D. Shin, *Appl. Surf. Sci.*, 2018, **444**, 10–14.
- 17 Z. D. Hood, H. Wang, A. S. Pandian, R. Peng, K. D. Gilroy, M. Chi, C. Liang and Y. Xia, *Adv. Energy Mater.*, 2018, **8**, 1800014.
- 18 S. Yubuchi, M. Uematsu, M. Deguchi, A. Hayashi and M. Tatsumisago, *ACS Appl. Energy Mater.*, 2018, **1**, 3622–3629.
- 19 B. Fan, Q. Zhang, Z. Luo, X. Zhang, H. Ma, P. Fan and B. Xue, *Solid State Ionics*, 2019, **343**, 115073.
- 20 N. H. H. Phuc, H. Muto and A. Matsuda, *Mater. Today: Proc.*, 2019, **16**, 216–219.
- 21 M. Takahashi, S. Yang, K. Yamamoto, K. Ohara, N. H. H. Phuc, T. Watanabe, T. Uchiyama, A. Sakuda, A. Hayashi, M. Tatsumisago, H. Muto, A. Matsuda and Y. Uchimoto, *Solid State Ion.*, 2021, **361**, 115568.
- 22 F. Strauss, J. Lin, J. Janek and T. Brezesinski, *Sci. Rep.*, 2021, **11**, 14073.
- 23 F. Marchini, B. Porcheron, G. Rousse, L. Albero Blanquer, L. Droguet, D. Foix, T. Koç, M. Deschamps and J. M. Tarascon, *Adv. Energy Mater.*, 2021, **11**, 2101111.
- 24 R. Maniwa, M. Calpa, N. C. Rosero-Navarro, A. Miura and K. Tadanaga, *J. Mater. Chem. A*, 2021, **9**, 400–405.
- 25 A. Ito, T. Kimura, A. Sakuda, M. Tatsumisago and A. Hayashi, *J. Sol-Gel Sci. Technol.*, 2022, **101**, 2–7.
- 26 H. Gamo, A. Nagai and A. Matsuda, *Sci. Rep.*, 2021, **11**, 21097.
- 27 S. Lu, F. Kosaka, S. Shiotani, H. Tsukasaki, S. Mori and J. Otomo, *Solid State Ion.*, 2021, **362**, 115583.
- 28 C. Yu, S. Ganapathy, J. Hageman, L. van Eijck, E. R. H. van Eck, L. Zhang, T. Schwietert, S. Basak, E. M. Kelder and M. Wagemaker, *ACS Appl. Mater. Interfaces*, 2018, **10**, 33296–33306.
- 29 Y. Seino, T. Ota, K. Takada, A. Hayashi and M. Tatsumisago, *Energy Environ. Sci.*, 2014, **7**, 627–631.