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## High Pressure Materials as Electrodes for Lithium Batteries: a Computational and Experimental Approach

E.M. Arroyo y de Dompablo<sup>a</sup>, U. Amador<sup>b</sup>

<sup>a</sup>Dept. Química Inorgánica Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid. <sup>b</sup>Dpt. Química, Fac. Farmacia, Universidad San Pablo-CEU, 28668 Boadilla del Monte, Madrid, Spain, E-mail: e.arroyo@quim.ucm.es

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Due to its superior electrochemical characteristics, most of the actual efforts on lithium batteries research focus on the lithium-iron phosphate  $\text{LiFePO}_4$  with olivine structure or on related materials which, nevertheless, show a poor electronic conductivity. On the other hand, under high pressure materials with dense and compact structures can be obtained: a relevant example in geology is the olivine to spinel transition in silicates. In this connection, high pressure seems to be an interesting way to enhance the electronic conductivity of materials as it modifies the band structure of solids by decreasing interatomic distances and promoting orbital overlapping. Along these lines we are exploring novel compounds of general formula  $\text{LiMXO}_4$  ( $X = \text{P, As}$ ) obtained under high pressure/high temperature conditions which could be suitable as host materials for lithium insertion-extraction reactions. We have found that some lithium arseniates with the olivine structure transform into spinels at 6 GPa and 1000°C but, under the same conditions olivine-like phosphates do not transform to the spinel but to materials with a  $\text{CrVO}_4$ -like structure. The electrochemical behaviour of olivine- $\text{LiMXO}_4$  ( $X = \text{P, As}$ ) and the high pressure polymorphs as positive electrode in lithium cells has been studied using a combination of experimental and first principle calculations methods.

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## Morphological insights into polymer electrolyte membranes from SAXS and maximum entropy

J.A. Elliott

Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ. E-mail: jae1001@cam.ac.uk

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Perfluorosulphonate ionomer membranes (PIMs) consist of a polymeric fluoropolymer backbone with pendant ionic side groups terminated by sulphonic acid moieties periodically substituted along the main chain, and are of great commercial interest due to their ion transport properties. In particular, under certain conditions, these membranes are selectively conductive, passing cations but not anions. This makes them ideal as efficient membrane separators in redox fuel cells. It has been known for some time that the properties of PIMs derive from the microscopic phase separation of ionic material and the fluorocarbon matrix. However the precise nature of this remains controversial. In this paper, we present data from small angle X-ray scattering (SAXS) [1] and molecular dynamics [2] studies, which provide convincing evidence that PIMs possess an ion-clustered morphology with a structural hierarchy. In particular, a model-independent reconstruction of the phase segregation between polar and non-polar material can be obtained via a maximum entropy interpretation of the SAXS data [3]. Such models are consistent with surface images of membranes taken with atomic force microscopy [4], and molecular dynamics simulations show that these types of structures demonstrate selective conductivity in the presence of an applied electric field. Furthermore, recent quantum chemical studies [5,6] of small fragments of ionic side chains extracted from classical molecular dynamics simulations indicate that the degree of proton dissociation and transfer to the aqueous phase is highly dependent on the separation of the side groups and conformation of the fluoropolymer backbone. On the basis of the preceding considerations, we make some predictions as to factors that may help to improve the performance of PIMs under conditions of minimal hydration.

- [1] J. A. Elliott and S. Hanna, *Journal of Applied Crystallography* 32, 1069 (1999).  
 [2] J. A. Elliott, S. Hanna, A. M. S. Elliott, et al., *Phys. Chem. Chem. Phys.* 1, 4855 (1999).  
 [3] J. A. Elliott, S. Hanna, A. M. S. Elliott et al., *Macromolecules* 33, 4161 (2000).  
 [4] P. J. James, J. A. Elliott, T. J. McMaster et al., *Journal of Materials Science*, 35, 5111 (2000).  
 [5] S. J. Paddison and J. A. Elliott, *J. Phys. Chem. A*, 109, 7583 (2005).  
 [6] S. J. Paddison and J. A. Elliott, *Phys. Chem. Chem. Phys.*, 18, 2133 (2006).