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## ***A study of sulfide-based solid electrolytes (SSEs) sensitivity towards humidity: gas evolution quantification and degradation mechanisms investigation***

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Lithium-ion batteries (LIBs) have been widely used for several energy storage applications (electronic devices, electric vehicles). However, their high flammable organic liquid electrolyte keep them from being used in high energy density batteries. A very promising alternative to LIBs are all-solid-state batteries (ASSBs) containing a sulfide-based solid electrolyte (SSE). SSEs have two main advantages, a high ionic conductivity and deformability [1, 2]. However, their main disadvantage is their high sensitivity towards humidity. In fact, SSEs can react with very low concentrations of water (down to a few tens ppm vol.), leading to the destruction of their structure and release of toxic H<sub>2</sub>S gas [3].

The aim of the present work is to characterize the reactivity of commercial SSEs (Li<sub>6</sub>PS<sub>5</sub>Cl, Li<sub>6</sub>PS<sub>5</sub>Br, Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>, Li<sub>3</sub>PS<sub>4</sub>, Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>) towards humidity in realistic dry room conditions. To do so, it is focused on two main aspects:

- Accurate quantification of gases generated by these SSEs when reacting with moisture via a homemade flow-through setup. The developed flow-through setup is more efficient than closed-type setups commonly used and described in literature [3, 4]. Indeed, it avoids overconcentration of detected gases frequently encountered when using closed-type setups;
- Investigation of SSEs degradation mechanisms thanks to characterizations of pristine and humidity-exposed SSEs.

Gas quantification experiments carried out for 22 hours on 1 g of SSE samples exposed to a dry room atmosphere (dew point, d. p. - 40°C) revealed two types of H<sub>2</sub>S evolution profiles depending on SE structure (Fig. 1):

A peak followed by a growing evolution of H<sub>2</sub>S was found for Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> and Li<sub>3</sub>PS<sub>4</sub>. We assume in this case a surface reaction between SSE and water molecules that result in the formation of a poor passivating layer on SSE particle surfaces. The passivating layer formed is inefficient in preventing humidity diffusion into the bulk of SSE powder, leading to a continuous SSE degradation.

A peak followed by a low plateau of H<sub>2</sub>S evolution was found for Li<sub>6</sub>PS<sub>5</sub>Cl, Li<sub>6</sub>PS<sub>5</sub>Br and Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>. In this case, the passivating layer formed on the surface of SE powders as a product of reaction with traces of water is efficient. It drastically reduces humidity diffusion into SSE powder bulk, generating very low amounts of H<sub>2</sub>S after the initial peak (diffusion-dependent plateau on the curve).

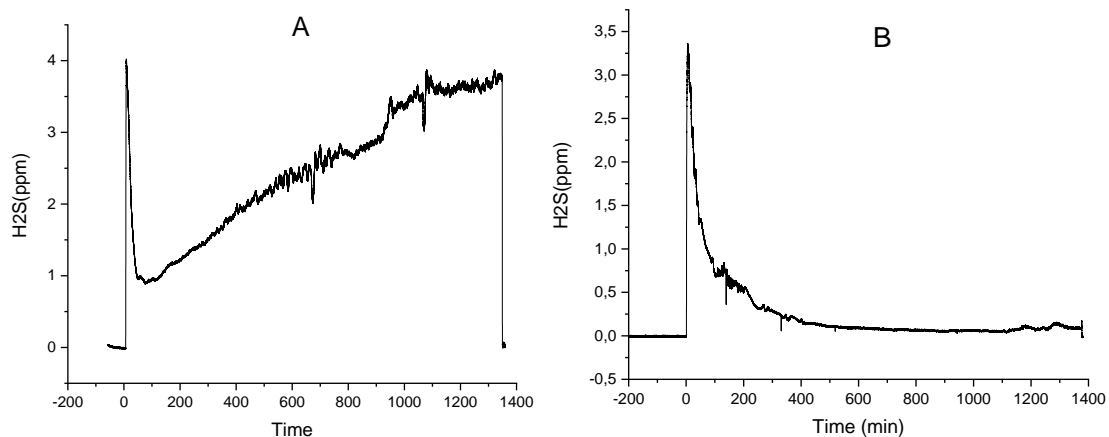


Fig. 1: H<sub>2</sub>S evolution profiles of 1g of SE samples exposed to a dry room atmosphere (d. p. - 40 °C) for 22 hours, (A): Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> and (B): Li<sub>6</sub>PS<sub>5</sub>Cl.

Physicochemical characterizations of SSE powders before and after exposure to humidity allow us to relate these H<sub>2</sub>S evolution profiles with the chemical processes involved. Raman and XPS results evidenced a destruction of conductive structural groups by water and appearance of new phases on SSE particle surfaces. More specifically, for Li<sub>6</sub>PS<sub>5</sub>Cl, the presence of Li<sub>2</sub>CO<sub>3</sub> acting as a passivation layer was detected after humidity exposure.

#### Refs

[1] *Energy Storage Mater.* **2018**, *14*, 58–74; [2] *Nano Energy* **2021**, *83*, 105858; [3] *Solid State Ion.* **2011**, *182* (1), 116–119; [4] *Chem. Mater.* **2020**, *32* (6), 2664–2672.