Electronic Supplementary Information (ESI)

## Systematic study of ionic conduction in silver iodide / mesoporous alumina composites 2: Effect of silver bromide doping

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**Fig. S1** (a) N<sub>2</sub> gas adsorption (closed circles) and desorption (open circles) isotherms of MPA at 77 K. (b) Pore size distribution of MPA obtained by applying the BJH method.



**Fig. S2** DSC profiles of **Br0** before heat treatment (a) and after heat treatment at (b) 400 °C, (c) 500 °C, and (d) 600 °C (red: 1st heating process, blue: 1st cooling process, green: 2nd heating process) (see Y. Fukui *et al.*, *Phys. Chem. Chem. Phys.* 2023, **25**, 25594–25602).



**Fig. S3** PXRD patterns of **Br0** (orange: before heat treatment, blue: heat treatment at 400 °C, green: heat treatment at 500 °C, red: heat treatment at 600 °C) along with simulated patterns (black thin lines) of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -AgI (from the top) (see Y. Fukui *et al.*, *Phys. Chem. Chem. Phys.* 2023, **25**, 25594–25602).



Fig. S4 SEM images of Br10 (a) before and (b) after heat treatment at 600 °C for 20 h.



**Fig. S5** Phase diagram of AgI-AgBr/MPA system (blue:  $\beta/\gamma$ -AgI<sub>ss</sub>, green:  $\beta/\gamma$ -AgI<sub>ss</sub> + AgBr<sub>ss</sub>, yellow:  $\alpha$ -AgI<sub>ss</sub> + AgBr<sub>ss</sub>, red:  $\alpha$ -AgI<sub>ss</sub>). The phase boundaries indicated by black dotted lines were defined when the molar ratio of  $\beta/\gamma$ -AgI<sub>ss</sub> or AgBr<sub>ss</sub> phase reaches 50% relative to that at 30 °C in (a) heating and (b) cooling processes (black circles). The ratios were determined by the Rietveld analysis of the variable-temperature PXRD patterns. The thin black lines represent the phase diagram of bulk AgI-AgBr system (H. Takahashi *et al., Solid State Ionics*, 1984, **14**, 107–112).



**Fig. S6** Temperature dependence of Nyquist plots of AgI-AgBr/MPA composites with various AgI:AgBr molar ratios ((a) **Br0**, (b) **Br1**, (c) **Br5**, (d) **Br10**, (e) **Br20**, and (f) **Br30**) at 25 °C (deep blue), 50 °C (light blue), 100 °C (green), 150 °C (yellow), and 200 °C (red) in the heating process.



Fig. S7 Plots of  $\sigma_{200^{\circ}C}$  against AgBr-doping ratio for AgI-AgBr/MPA composites.



Fig. S8 Temperature dependence of the lattice parameters of (a) cubic  $\alpha$ -AgI<sub>ss</sub> phase in Br10 (green), Br20 (blue), and Br30 (purple) and (b) cubic AgBr<sub>ss</sub> phase in Br30 determined by the Rietveld analysis of the variable-temperature PXRD patterns in the cooling process.



Fig. S9 PXRD patterns of Br0 before (bottom) and after (top) the electrochemical impedance spectroscopy measurements (25–200 °C) (see Y. Fukui *et al.*, *Phys. Chem. Chem. Phys.* 2023, 25, 25594–25602).



**Fig. S10** Schematic illustrations to explain the Ag<sup>+</sup>-ion conducting behaviour of AgI-AgBr/MPA composites by varying the AgBr content.



**Fig. S11** SEM images and EDS mappings (Overlay, Al, Ag, I, and Br) of **Br20** (a) before and (b) after heat treatment at 600 °C for 20 h.



Fig. S12  $N_2$  gas adsorption (closed circles) and desorption (open circles) isotherms of Br20 (a) before and (b) after heat treatment at 600 °C for 20 h.



Fig. S13 SEM images of Br20 (a) before and (b) after heat treatment at 600 °C for 20 h.