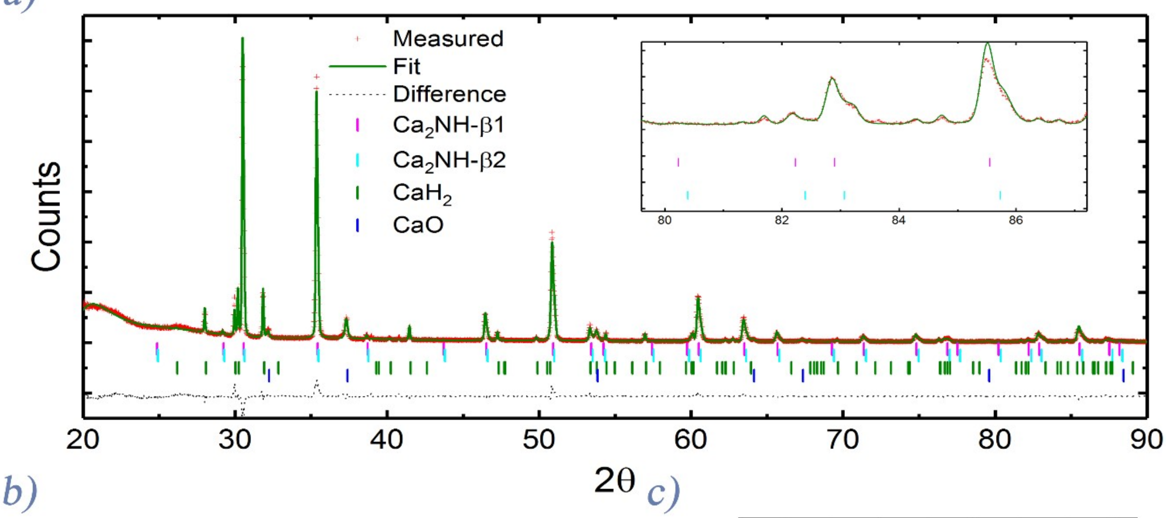
Electronic Supplementary Material (ESI) for Faraday Discussions.

SUPPLEMENTAL INFORMATION:

Ionic conductivity and disorder in calcium and barium nitrogen hydrogen phases

Gavin J. Irvine* and John TS Irvine*

a)



b)

XRD RT	Ca_2NH-β1	Ca_2NH-β2	Brice et al.	Sichla et al.
a	10.15316(23)	10.1280(9)	10.13	5.14
Ca (x,x,x)				*Fm-3m (Imide)*
x	0.26091(1)	0.2599(1)	0.26	0
occ	1	1	1	1
N1 (½,½,½)				
occ	1	1	1	1
wt %	0.500(8)	0.316(1)		

c)

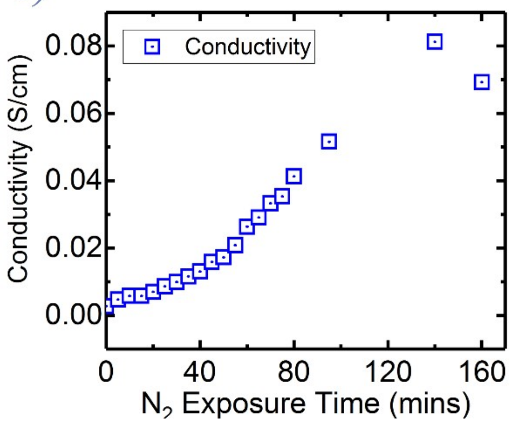
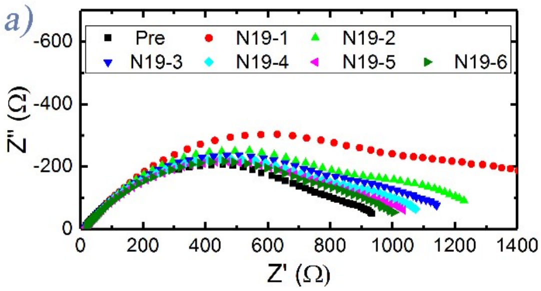


Figure S1: CaH_2+N_2 at 600 °C PXRD pattern refinement and EIS data as a function of exposure time. In contrast to Ca_2NH formed from Ca_2N, the ionic conductivity (σ) starts off small (4×10^{-3} S/cm) before slowly climbing to maximum value of 0.08 S/cm. We can see that further exposure time past approximately 150 mins actually causes σ to drop by about 12.5%. This drop is associated with the presence of shoulder peaks in the post experiment PXRD pattern. Reference patterns are from Brice et al and Sichla et al[1], [2].

*gji4@st-andrews.ac.uk; jtsi@st-andrews.ac.uk



b)

Run	Rs (Ω)	Rp_1 (Ω)	Cp_1 (μF)	Rp_2 (Ω)	Cp_2 (nF)
Pre	11.12(46)	239(148)	68(19)	734(99)	4.3(4)
N19-1	15.48(50)	610(186)	53(16)	1054(97)	2.7(2)
N19-2	15.13(51)	412(107)	56(19)	883(59)	2.6(2)
N19-3	14.52(51)	365(135)	51(18)	834(85)	3.2(2)
N19-4	14.06(53)	311(119)	61(24)	809(75)	2.9(2)
N19-5	13.67(53)	289(145)	67(29)	790(93)	3.2(2)
N19-6	13.62(54)	252(141)	64(29)	787(98)	3.2(2)

Figure S2: Nyquist data from the CaH_2+N_2 experiment for the 19th dose of nitrogen (N19). The number after the dash represents the order in which the scans were collected. They were collected in 5 min increments. The data show that exposure to N_2 is associated with a dramatic increase in the charge transfer process (electrode, μF, and surface, *nF*)[3], while the bulk conductivity (Rs) originally decreases, before recovering albeit not entirely. This decreases in bulk performance is associated with shoulder peak formation.

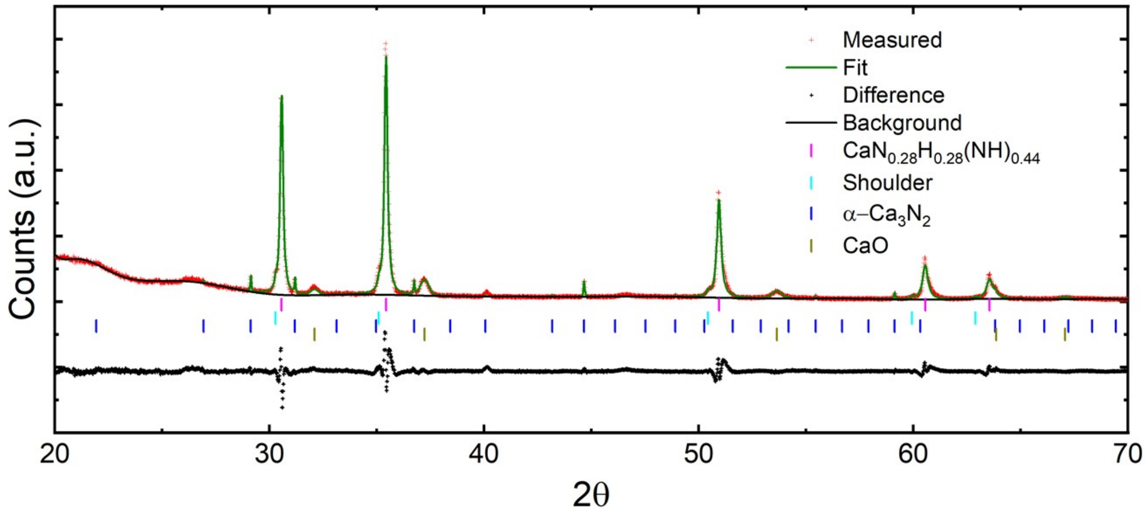


Figure S3: XRD Pattern and refinement of an α-Ca_2NH phase formed by exposing an α-Ca_3N_2 pellet to 5/5/90 cm^3/min N_2/H_2/Ar at 600 °C. The pattern shows the characteristic shoulder peaks of a secondary species for a Ca_2NH phase. Additionally, the refinement showed that the optimum Ca:N ratio was 2:1.44, which gives an imide concentration of 44%, which is higher than found in a neutron diffraction experiment[4]. This result implies that difference in synthesis conditions gives rise to different amounts of secondary species. However, since, H-species, are all but invisible in XRD, the result is far from certain and warrants further exploration.

*gji4@st-andrews.ac.uk; jtsi@st-andrews.ac.uk

Phase	Nitride-hydride phase	Shoulder
Space Group	Fm-3m	Fm-3m
a (Å)	5.07200(25)	5.1191(6)
V ($Å^3$)	130.475(11)	134.150(26)
Ca (0 0 0)		
Uiso ($Å^2$)	1.94(11)	0
N (½ ½ ½)		
frac	0.722	1
Uiso	0	0
X^2	4.82	
Rp	0.0830	
Rwp	0.115	

Table S1: Refinement results for figure S3. CaO and α-Ca_3N_2 refinement results gave lattice parameters of 4.834 Å and 11.484608 Å respectively, while the other parameters remained those of the published literature[5], [6].

References:

[1] J. F. Brice, J. P. Motte, A. Courtois, J. Protas, and J. Aubry, “Etude structurale de Ca2NH par diffraction des rayons X, diffraction des neutrons et resonance magnetique nuclaire du proton dans le solide,” *J. Solid State Chem.*, vol. 17, no. 1–2, pp. 135–142, 1976, doi: 10.1016/0022-4596(76)90213-9.

[2] T. SICHLA and H. JACOBS, “ChemInform Abstract: Synthesis and Crystal Structure of Calcium Imide, CaNH.,” *ChemInform*, 2010, doi: 10.1002/chin.199714007.

[3] J. T. S. Irvine, D. C. Sinclair, and A. R. West, “Electroceramics: characterization by impedance spectroscopy,” *Adv. Mater.*, vol. 2, no. 3, pp. 132–138, 1990, doi: 10.1002/adma.19900020304.

[4] G. J. Irvine, M. Owen Jones, and J. T. Irvine, “Ionic conductivity dependence on composition and structure in calcium nitride hydride systems,” *Submitt. Publ.*, no. submitted, 2022.

[5] C. H. Shen, R. S. Liu, J. G. Lin, and C. Y. Huang, “Phase stability study of $La_{1.2}Ca_{1.8}Mn_2O_7$,” *Mater. Res. Bull.*, vol. 36, pp. 1139–1148, 2001.

[6] O. Reckeweg and F. J. DiSalvo, “About binary and ternary alkaline earth metal nitrides,” *Zeitschrift für Anorg. und Allg. Chemie*, vol. 627, no. 3, pp. 371–377, Mar. 2001, doi: 10.1002/1521-3749(200103)627:3<371::AID-ZAAC371>3.0.CO;2-A.

*gji4@st-andrews.ac.uk; jtsi@st-andrews.ac.uk