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Journal of Electroanalytical Chemistry 476 (1999) 92–93

JOURNAL OF ELECTROANALYTICAL CHEMISTRY

Short Communication

The electrolysis of water

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Received 17 May 1999; received in revised form 13 August 1999; accepted 13 August 1999

In a lively, enjoyable tribute to Alessandro Volta, Professor Trasatti [1] recalls the stimulating effect Volta's invention of a working battery had on science at the beginning of the nineteenth century. This note will not take anything away from that, but merely add a small historical detail. Repeating a widely quoted myth, Prof. Trasatti wrote [1] that Nicholson and Carlisle 'discovered water electrolysis'. That is not quite correct, since water electrolysis had been discovered and properly interpreted more than a decade earlier, by two Dutchmen, Paets van Troostwijk and Deiman. Moreover, Nicholson was keenly aware of their work. Just as Professor Trasatti writes about his countryman, let me do so about mine.

Adriaan Paets van Troostwijk (1752–1837) was a merchant in Amsterdam, and his friend Johan Rudolph Deiman (1743–1808) was a medical doctor there. They used a glass tube closed at its bottom, where a thin gold wire protruded through the glass. The tube was filled with water and, under water, inverted. Another thin gold wire was then inserted through the open end, and came to within a short distance of the sealed-in wire. The wires were connected to a powerful electrostatic generator based on friction. The electric discharges of the generator caused gas evolution on both wires. The gas collected in the closed end of the tube, and thereby pushed the water level down. Once enough gas had collected in the tube to make the top gold wire lose contact with the water, the next discharge would cause a spark through the gas, which then recombined explosively to water, whereupon the experiment could be repeated. Cavendish had already demonstrated [2] that an electric spark would convert a 2:1 mixture of hydrogen and oxygen into water, and Paets van Troostwijk and Deinum therefore concluded that they had made just such a gas mixture.

Paets van Troostwijk and Deiman published their experiment, and its interpretation, in French [3], German [4], and Dutch [5], and their results were soon confirmed by Gren [6]. They were also known in England: Pearson duplicated them, as he reported to the Royal Society (of which he was a fellow) on February 2, 1797. His account, printed in the Philosophical Transactions [7], concluded that 'The evidence contained under the heads (a)–(e), considered singly and conjunctively, I apprehend, must be admitted by the most rigorous reasoner, to be demonstrative that hydrogen and oxygen gaz were produced by passing electric discharges through water.'

Nicholson republished Pearson's paper in his own journal, in three successive installments [8], and also contributed comments on the German translation of that paper [9]. There can therefore be no doubt that Nicholson was aware of the results of the two Dutchmen, and was thus well-prepared to repeat their water electrolysis experiment. Volta's battery provided a much more convenient direct voltage, which made it possible to analyze the anodic and cathodic electrolysis products separately. Still, Nicholson [10,11] already knew what to expect, and he fully confirmed the Dutch results.

The interested reader can find a detailed description of the experiments of Paets van Troostwijk and Deiman in Ostwald's textbook on electrochemistry and its history [12]. An extensive discussion of its historical context, and on its role in winning phlogistonists over to the chemical theory of Lavoisier, was presented by Snelders [13].

Of course, Volta provided an inexpensive and easily reproducible source of near-constant voltage, whereas an electrostatic generator was cumbersome, not generally available, and produced oscillatory spark discharges. Thus, electrochemistry indeed took off with Volta's invention. But the electrolysis of water had been

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PII: S0022-0728(99)00365-4

achieved, and correctly interpreted, well before that invention. In fact, the 1789 water electrolysis experiment stands, together with Galvani's contemporaneous findings, and Volta's subsequent battery, as one of the three founding events of electrochemistry.

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